

CHAPTER

1

# The Nature of Physical Chemistry and the Kinetic Theory of Gases

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LAIDLER . MEISER . SANCTUARY

## Physical Chemistry

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# Problems and Solutions

## Chapter 1

*\*problems with an asterisk are slightly more demanding*

### Classical Mechanics and Thermal Equilibrium

- 1.1.** Calculate the amount of work required to accelerate a 1000-kg car (typical of a Honda Civic) to  $88 \text{ km hr}^{-1}$  (55 miles  $\text{hr}^{-1}$ ). Compare this value to the amount of work required for a 1600-kg car (typical of a Ford Taurus) under the same conditions.

[Solution](#)

- 1.2.** Assume that a rod of copper is used to determine the temperature of some system. The rod's length at  $0^\circ\text{C}$  is 27.5 cm, and at the temperature of the system it is 28.1 cm. What is the temperature of the system? The linear expansion of copper is given by an equation of the form  $l_t = l_0(1 + \alpha t + \beta t^2)$  where  $\alpha = 0.160 \times 10^{-4} \text{ K}^{-1}$ ,  $\beta = 0.10 \times 10^{-7} \text{ K}^{-2}$ ,  $l_0$  is the length at  $0^\circ\text{C}$ , and  $l_t$  is the length at  $t^\circ\text{C}$ .

[Solution](#)

- 1.3.** Atoms can transfer kinetic energy in a collision. If an atom has a mass of  $1 \times 10^{-24} \text{ g}$  and travels with a velocity of  $500 \text{ m s}^{-1}$ , what is the maximum kinetic energy that can be transferred from the moving atom in a head-on elastic collision to the stationary atom of mass  $1 \times 10^{-23} \text{ g}$ ?

[Solution](#)

- 1.4.** Power is defined as the rate at which work is done. The unit of power is the watt ( $\text{W} = 1 \text{ J s}^{-1}$ ). What is the power that a man can expend if all his food consumption of 8000 kJ a day ( $\approx 2000 \text{ kcal}$ ) is his only source of energy and it is used entirely for work?

[Solution](#)

- 1.5.** State whether the following properties are intensive or extensive: (a) mass; (b) density; (c) temperature; (d) gravitational field.

[Solution](#)

## Gas Laws and Temperature

- 1.6.** The mercury level in the left arm of the J-shaped tube in Fig. 1.6a is attached to a thermostat gas-containing bulb. The left arm is 10.83 cm and the right arm is 34.71 cm above the bottom of the manometer. If the barometric pressure reads 738.4 Torr, what is the pressure of the gas? Assume that temperature-induced changes in the reading of the barometer and J tube are small enough to neglect.

[Solution](#)

- 1.7.** Vacuum technology has become increasingly more important in many scientific and industrial applications. The unit Torr, defined as 1/760 atm, is commonly used in the measurement of low pressures.

**a.** Find the relation between the older unit mmHg and the Torr. The density of mercury is  $13.5951 \text{ g cm}^{-3}$  at  $0.0^\circ\text{C}$ . The standard acceleration of gravity is defined as  $9.80665 \text{ m s}^{-2}$ .

**b.** Calculate at 298.15 K the number of molecules present in  $1.00 \text{ m}^3$  at  $1.00 \times 10^{-6}$  Torr and at  $1.00 \times 10^{-15}$  Torr (approximately the best vacuum obtainable).

[Solution](#)

- 1.8.** The standard atmosphere of pressure is the force per unit area exerted by a 760-mm column of mercury, the density of which is  $13.59511 \text{ g cm}^{-3}$  at  $0^\circ\text{C}$ . If the gravitational acceleration is  $9.80665 \text{ m s}^{-2}$ , calculate the pressure of 1 atm in kPa.

[Solution](#)

- 1.9.** Dibutyl phthalate is often used as a manometer fluid. Its density is  $1.047 \text{ g cm}^{-3}$ . What is the relationship between 1.000 mm in height of this fluid and the pressure in torr?

[Solution](#)

- 1.10.** The volume of a vacuum manifold used to transfer gases is calibrated using Boyle's law. A  $0.251\text{-dm}^3$  flask at a pressure of 697 Torr is attached, and after system pumpdown, the manifold is at 10.4 Torr. The stopcock between the manifold and flask is opened and the system reaches an equilibrium pressure of 287 Torr. Assuming isothermal conditions, what is the volume of the manifold?

[Solution](#)

- 1.11.** An ideal gas occupies a volume of  $0.300 \text{ dm}^3$  at a pressure of  $1.80 \times 10^5 \text{ Pa}$ . What is the new volume of the gas maintained at the same temperature if the pressure is reduced to  $1.15 \times 10^5 \text{ Pa}$ ?

[Solution](#)

**1.12.** If the gas in Problem 1.11 were initially at 330 K, what will be the final volume if the temperature were raised to 550 K at constant pressure?

[Solution](#)

**1.13.** Calculate the concentration in  $\text{mol dm}^{-3}$  of an ideal gas at 298.15 K and at (a) 101.325 kPa (1 atm), and (b)  $1.00 \times 10^{-4}$  Pa ( $= 10^{-9}$  atm). In each case, determine the number of molecules in  $1.00 \text{ dm}^3$ .

[Solution](#)

**\*1.14.** A J-shaped tube is filled with air at 760 Torr and 22 °C. The long arm is closed off at the top and is 100.0 cm long; the short arm is 40.00 cm high. Mercury is poured through a funnel into the open end. When the mercury spills over the top of the short arm, what is the pressure on the trapped air? Let  $h$  be the length of mercury in the long arm.

[Solution](#)

**1.15.** A Dumas experiment to determine molar mass is conducted in which a gas sample's  $P$ ,  $\theta$ , and  $V$  are determined. If a 1.08-g sample is held in  $0.250 \text{ dm}^3$  at 303 K and 101.3 kPa:

a. What would the sample's volume be at 273.15 K, at constant pressure?

b. What is the molar mass of the sample?

[Solution](#)

**1.16.** A gas that behaves ideally has a density of  $1.92 \text{ g dm}^{-3}$  at 150 kPa and 298 K. What is the molar mass of the sample?

[Solution](#)

**1.17.** The density of air at 101.325 kPa and 298.15 K is  $1.159 \text{ g dm}^{-3}$ . Assuming that air behaves as an ideal gas, calculate its molar mass.

[Solution](#)

**1.18.** A  $0.200\text{-dm}^3$  sample of  $\text{H}_2$  is collected over water at a temperature of 298.15 K and at a pressure of 99.99 kPa. What is the pressure of hydrogen in the dry state at 298.15 K? The vapor pressure of water at 298.15 K is 3.17 kPa.

[Solution](#)



- 1.19.** What are the mole fractions and partial pressures of each gas in a 2.50-L container into which 100.00 g of nitrogen and 100.00 g of carbon dioxide are added at 25 °C? What is the total pressure?

[Solution](#)

- 1.20.** The decomposition of  $\text{KClO}_3$  produces 27.8 cm<sup>3</sup> of  $\text{O}_2$  collected over water at 27.5 °C. The vapor pressure of water at this temperature is 27.5 Torr. If the barometer reads 751.4 Torr, find the volume the dry gas would occupy at 25.0 °C and 1.00 bar.

[Solution](#)

- 1.21.** Balloons now are used to move huge trees from their cutting place on mountain slopes to conventional transportation. Calculate the volume of a balloon needed if it is desired to have a lifting force of 1000 kg when the temperature is 290 K at 0.940 atm. The balloon is to be filled with helium. Assume that air is 80 mol %  $\text{N}_2$  and 20 mol %  $\text{O}_2$ . Ignore the mass of the superstructure and propulsion engines of the balloon.

[Solution](#)

- \*1.22.** A gas mixture containing 5 mol % butane and 95 mol % argon (such as is used in Geiger-Müller counter tubes) is to be prepared by allowing gaseous butane to fill an evacuated cylinder at 1 atm pressure. The 40.0-dm<sup>3</sup> cylinder is then weighed. Calculate the mass of argon that gives the desired composition if the temperature is maintained at 25.0 °C. Calculate the total pressure of the final mixture. The molar mass of argon is 39.9 g mol<sup>-1</sup>.

[Solution](#)

- 1.23.** The gravitational constant  $g$  decreases by 0.010 m s<sup>-2</sup> km<sup>-1</sup> of altitude.

**a.** Modify the barometric equation to take this variation into account. Assume that the temperature remains constant.

**b.** Calculate the pressure of nitrogen at an altitude of 100 km assuming that sea-level pressure is exactly 1 atm and that the temperature of 298.15 K is constant.

[Solution](#)

- 1.24.** Suppose that on another planet where the atmosphere is ammonia that the pressure on the surface, at  $h = 0$ , is 400 Torr at 250 K. Calculate the pressure of ammonia at a height of 8000 metres. The planet has the same  $g$  value as the earth.

[Solution](#)

- 1.25.** Pilots are well aware that in the lower part of the atmosphere the temperature decreases linearly with altitude. This dependency may be written as  $T = T_0 - az$ , where  $a$  is a proportionality constant,  $z$  is the altitude, and  $T_0$  and  $T$  are the temperatures at ground level and at altitude  $z$ , respectively. Derive an expression for the barometric equation that takes this into account. Work to a form involving  $\ln P/P_0$ .

[Solution](#)

- 1.26.** An ideal gas thermometer and a mercury thermometer are calibrated at 0 °C and at 100 °C. The thermal expansion coefficient for mercury is

$$\alpha = \frac{1}{V_0} (\partial V / \partial T)_p$$
$$= 1.817 \times 10^{-4} + 5.90 \times 10^{-9} \theta + 3.45 \times 10^{-10} \theta^2$$

where  $\theta$  is the value of the Celsius temperature and  $V_0 = V$  at  $\theta = 0$ . What temperature would appear on the mercury scale when the ideal gas scale reads 50 °C?

[Solution](#)

### Graham's Law, Molecular Collisions, and Kinetic Theory

- 1.27.** It takes gas A 2.3 times as long to effuse through an orifice as the same amount of nitrogen. What is the molar mass of gas A?

[Solution](#)

- 1.28.** Exactly 1 dm<sup>3</sup> of nitrogen, under a pressure of 1 bar, takes 5.80 minutes to effuse through an orifice. How long will it take for helium to effuse under the same conditions?

[Solution](#)

- 1.29.** What is the total kinetic energy of 0.50 mol of an ideal monatomic gas confined to 8.0 dm<sup>3</sup> at 200 kPa?

[Solution](#)

- 1.30.** Nitrogen gas is maintained at 152 kPa in a 2.00-dm<sup>3</sup> vessel at 298.15 K. If its molar mass is 28.0134 g mol<sup>-1</sup> calculate:

- The amount of N<sub>2</sub> present.
- The number of molecules present.

- c. The root-mean-square speed of the molecules.
- d. The average translational kinetic energy of each molecule.
- e. The total translational kinetic energy in the system.

[Solution](#)

**1.31.** By what factor are the root-mean-square speeds changed if a gas is heated from 300 K to 400 K?

[Solution](#)

**\*1.32.** The collision diameter of  $\text{N}_2$  is  $3.74 \times 10^{-10}$  m at 298.15 K and 101.325 kPa. Its average speed is  $474.6 \text{ m s}^{-1}$ . Calculate the mean free path, the average number of collisions  $Z_A$  experienced by one molecule in unit time, and the average number of collisions  $Z_{AA}$  per unit volume per unit time for  $\text{N}_2$ .

[Solution](#)

**\*1.33.** Express the mean free path of a gas in terms of the variables pressure and temperature, which are more easily measured than the volume.

[Solution](#)

**1.34.** Calculate  $Z_A$  and  $Z_{AA}$  for argon at 25 °C and a pressure of 1.00 bar using  $d = 3.84 \times 10^{-10}$  m obtained from X-ray crystallographic measurements.

[Solution](#)

**1.35.** Calculate the mean free path of Ar at 20 °C and 1.00 bar. The collision diameter  $d = 3.84 \times 10^{-10}$  m.

[Solution](#)

**1.36.** Hydrogen gas has a molecular collision diameter of 0.258 nm. Calculate the mean free path of hydrogen at 298.15 K and (a) 133.32 Pa, (b) 101.325 k Pa, and (c)  $1.0 \times 10^8$  Pa.

[Solution](#)

**1.37.** In interstellar space it is estimated that atomic hydrogen exists at a concentration of one particle per cubic meter. If the collision diameter is  $2.5 \times 10^{-10}$  m, calculate the mean free path  $\lambda$ . The temperature of interstellar space is 2.7 K.

[Solution](#)

- \*1.38.** Calculate the value of Avogadro's constant from a study made by Perrin [*Ann. Chem. Phys.*, 18, 1(1909)] in which he measured as a function of height the distribution of bright yellow colloidal gamboge (a gum resin) particles suspended in water. Some data at 15 °C are:

height, $z/10^{-6}$	5	35
$N$ , relative number of gamboge particles at height $z$	100	47
$\rho_{\text{gamboge}} = 1.206 \text{ g cm}^{-3}$		
$\rho_{\text{water}} = 0.999 \text{ g cm}^{-3}$ radius of gamboge particles, $r = 0.212 \times 10^{-6} \text{ m}$		

(Hint: Consider the particles to be gas molecules in a column of air and that the number of particles is proportional to the pressure.)

[Solution](#)

### Distributions of Speeds and Energies

- 1.39.** Refer to Table 1.3 (p. 32) and write expressions and values for (a) the ratio  $\sqrt{\overline{u^2}}/\bar{u}$ , and (b) the ratio  $\bar{u}/u_{mp}$ . Note that these ratios are independent of the mass and the temperature. How do the *differences* between them depend on these quantities?

[Solution](#)

- 1.40.** The speed that a body of any mass must have to escape from the earth is  $1.07 \times 10^4 \text{ m s}^{-1}$ . At what temperature would the average speed of (a) an  $\text{H}_2$  molecule, and (b) an  $\text{O}_2$  molecule be equal to this escape speed?

[Solution](#)

- 1.41.** **a.** For  $\text{H}_2$  gas at 25 °C, calculate the ratio of the fraction of molecules that have a speed  $2u$  to the fraction that have the average speed  $\bar{u}$ . How does this ratio depend on the mass of the molecules and the temperature?
- b.** Calculate the ratio of the fraction of the molecules that have the average speed  $\bar{u}_{100^\circ\text{C}}$  at 100 °C to the fraction that have the average speed  $\bar{u}_{25^\circ\text{C}}$  at 25 °C. How does this ratio depend on the mass?

[Solution](#)

- 1.42.** Suppose that two ideal gases are heated to different temperatures such that their pressures and vapor densities are the same. What is the relationship between their average molecular speeds?

[Solution](#)

- 1.43.** a. If  $\bar{u}_{25^\circ\text{C}}$  is the average speed of the molecules in a gas at  $25^\circ\text{C}$ , calculate the ratio of the fraction that will have the speed  $\bar{u}_{25^\circ\text{C}}$  at  $100^\circ$  to the fraction that will have the same speed at  $25^\circ\text{C}$ .  
b. Repeat this calculation for a speed of  $10 \bar{u}_{25^\circ\text{C}}$ .

[Solution](#)

- 1.44.** On the basis of Eq. 1.80 with  $\beta = 1/k_B T$ , derive an expression for the fraction of molecules in a one-dimensional gas having speeds between  $u_x$  and  $u_x + du_x$ . What is the most probable speed?

[Solution](#)

- \*1.45.** Derive an expression for the fraction of molecules in a one-dimensional gas having energies between  $\epsilon_x$  and  $\epsilon_x + d\epsilon_x$ . Also, obtain an expression for the average energy  $\bar{\epsilon}_x$ .

[Solution](#)

- \*1.46.** Derive an expression for the fraction of molecules in a two-dimensional gas having speeds between  $u$  and  $u + du$ . (*Hint:* Proceed by analogy with the derivation of Eq. 1.91.) Then obtain the expression for the fraction having energies between  $\epsilon$  and  $\epsilon + d\epsilon$ . What fraction will have energies in excess of  $\epsilon^*$ ?

[Solution](#)

### Real Gases

- 1.47.** In Section 1.13 it was stated that the van der Waals constant  $b$  is approximately four times the volume occupied by the molecules themselves. Justify this relationship for a gas composed of spherical molecules.

[Solution](#)

- 1.48.** Draw the van der Waals  $PV$  isotherm over the same range of  $P$  and  $V$  as in Figure 1.21 at  $350\text{ K}$  and  $450\text{ K}$  for  $\text{Cl}_2$  using the values in Table 1.4.

[Solution](#)

- 1.49.** Compare the pressures predicted for 0.8 dm<sup>3</sup> of Cl<sub>2</sub> weighing 17.5 g at 273.15 K using (a) the ideal gas equation and (b) the van der Waals equation.

[Solution](#)

- 1.50.** A particular mass of N<sub>2</sub> occupies a volume of 1.00 L at –50 °C and 800 bar. Determine the volume occupied by the same mass of N<sub>2</sub> at 100 °C and 200 bar using the compressibility factor for N<sub>2</sub>. At –50 °C and 800 bar it is 1.95; at 100 °C and 200 bar it is 1.10. Compare this value to that obtained from the ideal gas law.

[Solution](#)

- 1.51.** A gas is found to obey the equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V}$$

where  $a$  and  $b$  are constants not equal to zero. Determine whether this gas has a critical point; if it does, express the critical constants in terms of  $a$  and  $b$ . If it does not, explain how you determined this and the implications for the statement of the problem.

[Solution](#)

- 1.52.** Ethylene (C<sub>2</sub>H<sub>4</sub>) has a critical pressure of  $P_c = 61.659$  atm and a critical temperature of  $T_c = 308.6$  K. Calculate the molar volume of the gas at  $T = 97.2$  °C and 90.0 atm using Figure 1.22. Compare the value so found with that calculated from the ideal gas equation.

[Solution](#)

- 1.53.** Assuming that methane is a perfectly spherical molecule, find the radius of one methane molecule using the value of  $b$  listed in Table 1.5.

[Solution](#)

- 1.54.** Determine the Boyle temperature in terms of constants for the equation of state:

$$PV_m = RT\{1 + 8/57(P/P_c)(T_c/T)[1 - 4(T_c/T)^2]\}$$

$R$ ,  $P_c$ , and  $T_c$  are constants.

[Solution](#)



- 1.55.** Establish the relationships between van der Waals parameters  $a$  and  $b$  and the virial coefficients  $B$  and  $C$  of Eq. 1.117 by performing the following steps:

a. Starting with Eq. 1.101, show that

$$\frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT} \frac{1}{V_m}.$$

b. Since  $V_m/(V_m - b) = (1 - b/V_m)^{-1}$ , and  $(1 - x)^{-1} = 1 + x + x^2 + \dots$ , expand  $(1 - b/V_m)^{-1}$  to the quadratic term and substitute into the result of part (a).

c. Group terms containing the same power of  $V_m$  and compare to Eq. 1.117 for the case  $n = 1$ .

d. What is the expression for the Boyle temperature in terms of van der Waals parameters?

[Solution](#)

- \*1.56.** Determine the Boyle temperature of a van der Waals gas in terms of the constants  $a$ ,  $b$ , and  $R$ .

[Solution](#)

- 1.57.** The critical temperature  $T_c$  of nitrous oxide ( $\text{N}_2\text{O}$ ) is  $36.5^\circ\text{C}$ , and its critical pressure  $P_c$  is 71.7 atm. Suppose that 1 mol of  $\text{N}_2\text{O}$  is compressed to 54.0 atm at 356 K. Calculate the reduced temperature and pressure, and use Figure 1.22, interpolating as necessary, to estimate the volume occupied by 1 mol of the gas at 54.0 atm and 356 K.

[Solution](#)

- 1.58.** At what temperature and pressure will  $\text{H}_2$  be in a corresponding state with  $\text{CH}_4$  at 500.0 K and 2.00 bar pressure? Given  $T_c = 33.2$  K for  $\text{H}_2$ , 190.6 K for  $\text{CH}_4$ ;  $P_c = 13.0$  bar for  $\text{H}_2$ , 46.0 bar for  $\text{CH}_4$ .

[Solution](#)

- \*1.59.** For the Dieterici equation, derive the relationship of  $a$  and  $b$  to the critical volume and temperature. [*Hint:* Remember that at the critical point  $(\partial P/\partial V)_T = 0$  and  $(\partial^2 P/\partial V^2)_T = 0$ .]

[Solution](#)



- 1.60.** In Eq. 1.103 a cubic equation has to be solved in order to find the volume of a van der Waals gas. However, reasonably accurate estimates of volumes can be made by deriving an expression for the compression factor  $Z$  in terms of  $P$  from the result of the previous problem. One simply substitutes for the terms  $V_m$  on the right-hand side in terms of the ideal gas law expression  $V_m = RT/P$ . Derive this expression and use it to find the volume of  $\text{CCl}_2\text{F}_2$  at  $30.0^\circ\text{C}$  and  $5.00$  bar pressure. What will be the molar volume computed using the ideal gas law under the same conditions?

[Solution](#)

- \*1.61.** A general requirement of all equations of state for gases is that they reduce to the ideal gas equation (Eq. 1.28) in the limit of low pressures. Show that this is true for the van der Waals equation.

[Solution](#)

- 1.62.** The van der Waals constants for  $\text{C}_2\text{H}_6$  in the older literature are found to be

$$a = 5.49 \text{ atm L}^2 \text{ mol}^{-2} \text{ and } b = 0.0638 \text{ L mol}^{-1}$$

Express these constants in SI units ( $\text{L} = \text{liter} = \text{dm}^3$ ).

[Solution](#)

- \*1.63.** Compare the values obtained for the pressure of  $3.00$  mol  $\text{CO}_2$  at  $298.15$  K held in a  $8.25\text{-dm}^3$  bulb using the ideal gas, van der Waals, Dieterici, and Beattie-Bridgeman equations. For  $\text{CO}_2$  the Dieterici equation constants are

$$a = 0.462 \text{ Pa m}^6 \text{ mol}^{-2},$$

$$b = 4.63 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

[Solution](#)

- \*1.64.** A gas obeys the van der Waals equation with  $P_c = 3.040 \times 10^6$  Pa ( $= 30$  atm) and  $T_c = 473$  K. Calculate the value of the van der Waals constant  $b$  for this gas.

[Solution](#)

- \*1.65.** Expand the Dieterici equation in powers of  $V_m^{-1}$  in order to cast it into the virial form. Find the second and third virial coefficients. Then show that at low densities the Dieterici and van der Waals equations give essentially the same result for  $P$ .

[Solution](#)

**Essay Questions**

- 1.66.** In light of the van der Waals equation, explain the liquefaction of gases.
- 1.67.** State the postulates of the kinetic molecular theory of gases.
- 1.68.** Eq. 1.22 defines the ideal-gas thermometer. Describe how an actual measurement would be made using such a thermometer starting with a fixed quantity of gas at a pressure of 150 Torr.

**Solutions**

- 1.1.** Calculate the amount of work required to accelerate a 1000-kg car (typical of a Honda Civic) to  $88 \text{ km hr}^{-1}$  ( $55 \text{ miles hr}^{-1}$ ). Compare this value to the amount of work required for a 1600-kg car (typical of a Ford Taurus) under the same conditions.

**Solution:**

Given: Car 1 (Civic):  $m = 1000 \text{ kg}$ ,  $\text{Speed} = 88 \text{ km hr}^{-1}$

Car 2 (Taurus):  $m = 1600 \text{ kg}$ ,  $\text{Speed} = 88 \text{ km hr}^{-1}$

Required: work required for the acceleration of each vehicle

Any type of work can be resolved through dimensional analysis as the application of a force through a distance;

$$w = \int_{l_0}^l F(l) dl$$

Recall that bodies in motion possess kinetic energy defined by;  $E_k = \frac{1}{2} mu^2$  where  $u$  is the velocity of the moving body and  $m$  is its mass. It is possible to determine the amount of work required for the acceleration of a moving body by applying Newton's Second Law to the work integral given above.

$$w = \int_{l_0}^l \mathbf{F}(l) \cdot d\mathbf{l} = \int_{t_0}^t \mathbf{F}(l) \cdot \frac{d\mathbf{l}}{dt} dt = \int_{t_0}^t \mathbf{F}(l) \cdot \mathbf{u} dt$$

Substitute;  $\mathbf{F} = m\mathbf{a} = m \frac{d\mathbf{u}}{dt}$

$$w = \int_{t_0}^t m \frac{d\mathbf{u}}{dt} \cdot \mathbf{u} dt = m \int_{u_0}^u \mathbf{u} \cdot d\mathbf{u} \rightarrow w = \int_{l_0}^l \mathbf{F}(l) \cdot d\mathbf{l} = \frac{1}{2} mu_1^2 - \frac{1}{2} mu_0^2 = E_{k_1} - E_{k_0}$$

Conversion of speed from  $\text{km hr}^{-1}$  to  $\text{m s}^{-1}$ :

$$\text{Speed} = 88 \text{ km hr}^{-1} \rightarrow 88 \frac{\cancel{\text{km}}}{\cancel{\text{h}}} \times \frac{1}{3600} \frac{\cancel{\text{h}}}{\text{s}} \times 10^3 \frac{\text{m}}{\cancel{\text{km}}} = 24.4 \text{ m s}^{-1}$$

Using the equation for work derived from Newton's 2<sup>nd</sup> Law (Civic):

$$w_{\text{Civic}} = \int_{l_0}^l \mathbf{F}(l) \cdot d\mathbf{l} = \frac{1}{2} m \mathbf{u}_1^2 - \frac{1}{2} m \mathbf{u}_0^2 = E_{k_1} - E_{k_0}$$

$$w_{\text{Civic}} = \frac{1}{2} (1000 \text{ kg})(24.4 \text{ m s}^{-1})^2 - \frac{1}{2} (1000 \text{ kg})(0 \text{ m s}^{-1})^2$$

$$w_{\text{Civic}} = 297\,680 \text{ J}$$

$$\boxed{w_{\text{Civic}} = 298 \text{ kJ}}$$

The same method can be applied to the second vehicle (Taurus):

$$w_{\text{Taurus}} = \int_{l_0}^l \mathbf{F}(l) \cdot d\mathbf{l} = \frac{1}{2} m \mathbf{u}_1^2 - \frac{1}{2} m \mathbf{u}_0^2 = E_{k_1} - E_{k_0}$$

$$w_{\text{Taurus}} = \frac{1}{2} (1600 \text{ kg})(24.4 \text{ m s}^{-1})^2 - \frac{1}{2} (1600 \text{ kg})(0 \text{ m s}^{-1})^2$$

$$w_{\text{Taurus}} = 476\,288 \text{ J}$$

$$\boxed{w_{\text{Taurus}} = 476 \text{ kJ}}$$

By comparing both values quantitatively, it is possible to see that the work required to accelerate a moving body is directly proportional to its mass.

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- 1.2.** Assume that a rod of copper is used to determine the temperature of some system. The rod's length at 0 °C is 27.5 cm, and at the temperature of the system it is 28.1 cm. What is the temperature of the system? The linear expansion of copper is given by an equation of the form  $l_t = l_0(1 + \alpha t + \beta t^2)$  where  $\alpha = 0.160 \times 10^{-4} \text{ K}^{-1}$ ,  $\beta = 0.10 \times 10^{-7} \text{ K}^{-2}$ ,  $l_0$  is the length at 0 °C, and  $l_t$  is the length at  $t$  °C.

**Solution:**

Given: Copper Rod:  $l = 27.5\text{cm}$ ,  $T = 0$  °C

Copper Rod in System:  $l = 28.1\text{cm}$

Linear expansion of copper:  $l_t = l_0(1 + \alpha t + \beta t^2)$  where  $\alpha = 0.160 \times 10^{-4} \text{ K}^{-1}$ ,  $\beta = 0.10 \times 10^{-7} \text{ K}^{-2}$ ,  $l_0$  is the length at 0 °C, and  $l_t$  is the length at  $t$  °C

Required: temperature of the system when the rod length equals 28.1cm

Let us define the temperature as  $t''$  and make all of the appropriate substitutions into the equation for the linear expansion of copper (starting temperature at zero degrees):

$$l_t = l_0(1 + \alpha t + \beta t^2)$$

$$28.1 = 27.5(1 + 0.160 \times 10^{-4} t'' + 0.100 \times 10^{-7} t''^2)$$

Simplify and rearrange:

$$\frac{28.1}{27.5} = \frac{\cancel{27.5}(1 + 0.160 \times 10^{-4} t'' + 0.100 \times 10^{-7} t''^2)}{\cancel{27.5}}$$

$$1.0218 - 1 = \cancel{1} + 0.160 \times 10^{-4} t'' + 0.100 \times 10^{-7} t''^2 - \cancel{1}$$

$$0.0218 = 0.160 \times 10^{-4} t'' + 0.100 \times 10^{-7} t''^2$$

$$0 = 0.100 \times 10^{-7} t''^2 + 0.160 \times 10^{-4} t'' - 0.0218$$

This can be rearranged to:

$$0.100 \times 10^{-7} x^2 + 0.160 \times 10^{-4} x - 0.0218 = 0$$

Where  $x = t''$  and the system can be solved using the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.160 \times 10^{-4} \pm \sqrt{(0.160 \times 10^{-4})^2 - 4(0.100 \times 10^{-7})(-0.0218)}}{2(0.100 \times 10^{-7})}$$

$$x = 879^\circ\text{C}$$

$$\boxed{t'' = 879^\circ\text{C}}$$

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- 1.3.** Atoms can transfer kinetic energy in a collision. If an atom has a mass of  $1 \times 10^{-24}$  g and travels with a velocity of  $500 \text{ m s}^{-1}$ , what is the maximum kinetic energy that can be transferred from the moving atom in a head-on elastic collision to the stationary atom of mass  $1 \times 10^{-23}$  g?

**Solution:**

Given: Atom 1:  $m_1 = 1 \times 10^{-24} \text{ g}$ ,  $u_1 = 500 \text{ m s}^{-1}$

Atom 2:  $m_2 = 1 \times 10^{-23} \text{ g}$ ,  $u_2 = 0 \text{ m s}^{-1}$

Required: Find  $E_k(\text{max})$  that can be transferred from atom 1 to atom 2

It is important to note that during elastic collisions, no energy is lost to the internal motion of the bodies involved. This means that the sums of the kinetic energy in addition to the sums of momentum remain the same before and after the collision. Therefore, there is no potential energy change of interaction between the bodies in collision.

Momentum:  $p = mu$

Kinetic Energy =  $E_k = \frac{1}{2}mu^2$

$$\text{Conservation of Momentum: } m_1u_1 + m_2u_2 = m_1u_1' + m_2u_2' \quad (1)$$

$$\text{Conservation of Energy: } \frac{1}{2}m_1u_1^2 + \frac{1}{2}m_2u_2^2 = \frac{1}{2}m_1u_1'^2 + \frac{1}{2}m_2u_2'^2 \quad (2)$$

Since  $u_2 = 0 \text{ m s}^{-1}$ , then we can simplify equation (1) to get:

$$m_1u_1 + \cancel{m_2u_2} = m_1u_1' + m_2u_2'$$

Rearrangement then gives:

$$u_1 = u_1' + \frac{m_2u_2'}{m_1} \rightarrow u_1' = u_1 - \frac{m_2u_2'}{m_1}$$

It is possible to substitute the above into equation (2) and solve for  $u_2'$ ;



$$u_2' = \frac{2u_1}{1 + \frac{m_2}{m_1}} \rightarrow u_2' = \frac{2(500 \text{ m s}^{-1})}{1 + \frac{1 \times 10^{-23} \text{ g}}{1 \times 10^{-24} \text{ g}}}$$

$$u_2' = 90.9 \text{ m s}^{-1}$$

Now this value can be used to find the kinetic energy of atom 2 after the collision. Remember to use SI units by converting grams to kilograms;

$$E_k = \frac{1}{2} m_2 u_2'^2$$

$$E_k = \frac{1}{2} (1 \times 10^{-26} \text{ kg})(90.9 \text{ m s}^{-1})^2$$

$$E_k = 4.13 \times 10^{-23} \text{ J}$$

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**1.4.** Power is defined as the rate at which work is done. The unit of power is the watt ( $W = 1 \text{ J s}^{-1}$ ). What is the power that a man can expend if all his food consumption of 8000 kJ a day ( $\approx 2000 \text{ kcal}$ ) is his only source of energy and it is used entirely for work?

**Solution:**

Given: Daily food consumption = 8000 kJ ( $\approx 2000 \text{ kcal}$ )

Required:  $P_{\text{one day}}$

Remember that power is defined as the rate at which work can be done meaning that;

$$P = \frac{dw}{dt}$$

Since the man's entire caloric intake is going toward work, then we can say that;

$$dw = 8000 \text{ kJ} = 8000 \times 10^3 \text{ J}$$

We are only considering the power exerted in a single day;

$$dt = 1 \text{ day} = 24 \text{ hrs}$$

$$dt = 24 \cancel{\text{hrs}} \left( \frac{60 \cancel{\text{min}}}{1 \cancel{\text{hr}}} \right) \left( \frac{60 \text{ s}}{1 \cancel{\text{min}}} \right) = 86\,400 \text{ s}$$

Power is measured by the Watt unit and  $1 \text{ Watt} = 1 \text{ J s}^{-1}$  (remember SI units!)

$$P = \frac{8000 \times 10^3 \text{ J}}{86\,400 \text{ s}} \rightarrow 92.59 \text{ J s}^{-1}$$

$$\boxed{P = 92.6 \text{ W}}$$

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**1.5.** State whether the following properties are intensive or extensive: (a) mass; (b) density; (c) temperature; (d) gravitational field.

**Solution:**

Given: (a) mass (b) density (c) temperature (d) gravitational field

Required: intensive or extensive?

It is first important to define the terms intensive and extensive in the context of physical chemistry.

**Intensive properties** (sometimes called ‘bulk property’) are considered to be physical properties of a system that do not depend on its size. This means that their value will not change when the quantity of the matter in the system becomes subdivided.

**Extensive properties** are the physical properties of a system that DO depend on its size and content. The values of extensive properties change with system subdivision. In addition, the ratio of two intensive properties yields an extensive one.

Now it is possible to classify the above properties:

*Mass* → is extensive as it is a measure of ‘how much’ is present in the system

*Density* → is intensive

\*\*note: mass and volume are extensive

*Temperature* → is intensive

*Gravitational Field* → is intensive

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- 1.6.** The mercury level in the left arm of the J-shaped tube in Fig. 1.6a is attached to a thermostat gas-containing bulb. The left arm is 10.83 cm and the right arm is 34.71 cm above the bottom of the manometer. If the barometric pressure reads 738.4 Torr, what is the pressure of the gas? Assume that temperature-induced changes in the reading of the barometer and J tube are small enough to neglect.

**Solution:**

Given: left arm = 10.83 cm, right arm = 34.71 cm, barometric pressure = 738.4 Torr

Required:  $P_{\text{gas}}$

First, we need to find the difference in heights between the two columns (left and right arms);

$$\text{Right arm} - \text{Left arm} = 34.71 \text{ cm} - 10.83 \text{ cm} = 23.88 \text{ cm}$$

It is important to note that since the arm is open to the atmosphere, this pressure must also be added to the barometric pressure.

$$1 \text{ mmHg} = 1 \text{ Torr and therefore } 23.88 \text{ cmHg} = 238.8 \text{ Torr}$$

The pressure of the gas is then found to be;

$$238.8 \text{ Torr} + 738.4 \text{ Torr} = 977.2 \text{ Torr}$$

$$\boxed{P_{\text{gas}} = 977.2 \text{ Torr}}$$

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**1.7.** Vacuum technology has become increasingly more important in many scientific and industrial applications. The unit Torr, defined as  $1/760$  atm, is commonly used in the measurement of low pressures.

**a.** Find the relation between the older unit mmHg and the Torr. The density of mercury is  $13.5951 \text{ g cm}^{-3}$  at  $0.0^\circ\text{C}$ . The standard acceleration of gravity is defined as  $9.80665 \text{ m s}^{-2}$ .

**b.** Calculate at  $298.15 \text{ K}$  the number of molecules present in  $1.00 \text{ m}^3$  at  $1.00 \times 10^{-6} \text{ Torr}$  and at  $1.00 \times 10^{-15} \text{ Torr}$  (approximately the best vacuum obtainable).

**Solution:**

Given: Mercury:  $\rho = 13.5951 \text{ g cm}^{-3}$ ,  $T = 0.0^\circ\text{C}$

$$\text{acceleration of gravity} = 9.80665 \text{ m s}^{-2}$$

Required: (a) State the relationship between mmHg and Torr

(b)  $N_A$  in  $V = 1.00 \text{ m}^3$

**a)** We should first define the system as a column of mercury with a  $1 \text{ m}^2$  cross-sectional area,  $0.001 \text{ m}$  in height, a volume of  $0.001 \text{ m}^3$ . Since we already have the density of mercury it is possible to determine the mass;

$$\rho = \frac{m}{V} \rightarrow m = \rho V$$

$$m = 13.5951 \text{ kg m}^{-3} \times 0.001 \text{ m}^3$$

Now for 1 mmHg in a column;

$$1 \text{ mmHg} = (\text{mass})(\text{density})(\text{acceleration of gravity})$$

$$1 \text{ mmHg} = (0.001 \text{ m}^3) (13.5951 \text{ kg m}^{-3}) (9.80665 \text{ m s}^{-2})$$

$$1 \text{ mmHg} = 0.1333 \text{ kg m s}^{-2}$$

Now since  $1 \text{ Torr} = 1 \text{ mmHg}$  and  $1 \text{ Torr} = 133.322 \text{ Pa}$  then we can see that;

$$1 \text{ mmHg} = 133.322\,387\,4 \text{ Pa}$$

By definition, 1 atmosphere = 101 325 Pa and 1 Torr = 1/760 atm then;

$$1 \text{ Torr} = \frac{1}{760}(101\,325 \text{ Pa}) = 133.322\,368\,4 \text{ Pa}$$

Therefore;

$$1 \text{ mmHg} = \frac{133.322\,387\,4}{133.322\,368\,4} = 1.000\,000\,14 \text{ Torr}$$

The Torr is now defined as 1 mmHg.

**b)** Calculate the *number of molecules* present in a volume of 1.00 m<sup>3</sup>:

$$T = 298.15 \text{ K}, P_1 = 1.00 \times 10^{-6} \text{ Torr and } P_2 = 1.00 \times 10^{-15} \text{ Torr}$$

Using the ideal gas law:  $PV = nRT$  we define  $n$  as  $n = \frac{N}{L}$  and rearrange to get;

$$PV = nRT$$

$$PV = \frac{NRT}{L} \quad \text{where } L \text{ is Avogadro's number and } N \text{ is the number of particles}$$

$$L = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{And the number density is defined as } \frac{N}{V} = \frac{PL}{RT}$$

Remember to make the conversion for pressure!  $P_1 = 1.00 \times 10^{-6} \text{ Torr}$ ;

$$\frac{N_1}{V} = \frac{P_1 L}{RT}$$

$$\frac{N_1}{V} = \frac{(1 \times 10^{-6} \text{ Torr}) \left( \frac{1 \text{ atm}}{760 \text{ Torr}} \right)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})} \times (101325 \text{ Pa atm}^{-1}) (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$\frac{N_1}{V} = 3.24 \times 10^{16} \text{ m}^{-3}$$

$$N_1 = (3.24 \times 10^{16} \text{ m}^{-3}) (1.00 \text{ m}^3) = 3.24 \times 10^{16} \text{ particles}$$

$$\boxed{N_1 = 3.24 \times 10^{16}}$$

$P_2 = 1.00 \times 10^{-15} \text{ Torr}$  using the same method as outlined above;

$$\frac{N_2}{V} = \frac{P_2 L}{RT}$$

$$\frac{N_2}{V} = \frac{(1 \times 10^{-15} \text{ Torr}) \left( \frac{1 \text{ atm}}{760 \text{ Torr}} \right)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})} \times (101325 \text{ Pa atm}^{-1}) (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$N_2 = (3.24 \times 10^7 \text{ m}^{-3}) (1.00 \text{ m}^3) = 3.24 \times 10^7 \text{ particles}$$

$$\boxed{N_2 = 3.24 \times 10^7}$$

This is still a substantial number!

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**1.8.** The standard atmosphere of pressure is the force per unit area exerted by a 760-mm column of mercury, the density of which is  $13.595\ 11\ \text{g cm}^{-3}$  at  $0\ ^\circ\text{C}$ . If the gravitational acceleration is  $9.806\ 65\ \text{m s}^{-2}$ , calculate the pressure of 1 atm in kPa.

**Solution:**

Given: Mercury:  $\rho = 13.595\ 11\ \text{g cm}^{-3}$ ,  $T = 0\ ^\circ\text{C}$ , *acceleration of gravity*  $= 9.806\ 65\ \text{m s}^{-2}$

Required:  $P_{\text{column}}$  (kPa)

Let us define the system as a column of mercury with a cross-sectional area of  $1\ \text{m}^2$ ,  $0.760\ \text{m}$  in height and a volume of  $0.760\ \text{m}^3$ . Since we have the density, it is possible to find the mass of mercury occupying the column;

$$\rho = \frac{m}{V}$$

$$m = \rho V = (13\ 595.1\ \text{kg m}^{-3})(0.760\ \text{m}^3)$$

$$m = 10\ 332\ \text{kg}$$

Mass multiplied by the gravitational acceleration produces a force (or weight)  $F = ma$  according to Newton's Law of Motion. The column's weight on the unit area then gives a pressure;

$$P_{\text{column}} = (\text{density})(\text{volume})(\text{acceleration of gravity})$$

$$P_{\text{column}} = (13\ 595.1\ \text{kg m}^{-3})(0.760\ \text{m}^3)(9.806\ 65\ \text{m s}^{-2})$$

$$P_{\text{column}} = 101\ 325\ \text{kg m s}^{-2}$$

Since  $1\ \text{Pa} = 1\ \text{kg m s}^{-2}$  then the pressure is 101.325 kPa.

$P_{\text{column}} = 101.325\ \text{kPa}$
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**1.9.** Dibutyl phthalate is often used as a manometer fluid. Its density is  $1.047 \text{ g cm}^{-3}$ . What is the relationship between 1.000 mm in height of this fluid and the pressure in torr?

**Solution:**

Given: Dibutyl phthalate:  $\rho = 1.047 \text{ g cm}^{-3}$

Required: The relationship between 1.000 mm of this manometer fluid and pressure (Torr)

When two different liquids are being compared at constant volume and temperature, it is important to note that their pressures will be proportional to their densities.

Therefore, it is possible to take the ratio of DBP and Hg densities in order to calculate the pressure associated with 1mm of DBP.

$$\frac{1\text{mmDBP}}{1\text{ mmHg}}$$

$$\frac{\rho_{\text{DBP}}}{\rho_{\text{Hg}}} \propto \frac{P_{\text{DBP}}}{P_{\text{Hg}}} \rightarrow \frac{P_{\text{DBP}}}{P_{\text{Hg}}} = \frac{1.047 \text{ g cm}^{-3}}{13.595 \text{ g cm}^{-3}}$$

$$\frac{P_{\text{DBP}}}{P_{\text{Hg}}} = 0.077$$

$$P_{\text{DBP}} = 0.077 \text{ Torr}$$

Thus, 1mm DBP is equivalent to 0.077 Torr using the fact that 1mmHg is equivalent to 1 Torr. We can also state that;

$$\frac{1 \text{ Torr}}{0.077 \text{ Torr mm}^{-1}} = 12.98 \text{ mm DBP}$$

$$\boxed{1 \text{ mm DBP} = 0.077 \text{ Torr}}$$

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**1.10.** The volume of a vacuum manifold used to transfer gases is calibrated using Boyle's law. A 0.251-dm<sup>3</sup> flask at a pressure of 697 Torr is attached, and after system pumpdown, the manifold is at 10.4 mTorr. The stopcock between the manifold and flask is opened and the system reaches an equilibrium pressure of 287 Torr. Assuming isothermal conditions, what is the volume of the manifold?

**Solution:**

Given:  $V_1 = 0.251 \text{ dm}^3$ ,  $P_1 = 697 \text{ Torr}$ ,  $P_{\text{pumpdown}} = 10.4 \text{ mTorr}$ ,  $P_{\text{eq}} = 287 \text{ Torr}$

Required:  $V_{\text{manifold}}$

Since we are working under isothermal conditions, Boyle's Law will apply. This law describes the product of pressure and volume for a closed system. In a closed system, the temperature and moles are constant, thus;

$$P_1 V_1 = P_2 V_2$$

$$P_1 V_1 + P_{\text{pumpdown}} V_2 = P_{\text{eq}} (V_2 + V_1)$$

$$(697 \text{ Torr})(0.251 \text{ dm}^3) + (0.0104 \text{ Torr}) V_2 = 287 \text{ Torr} (V_2 + 0.251 \text{ dm}^3)$$

$$174.947 \text{ Torr dm}^3 + (0.0104 \text{ Torr}) V_2 = (287 \text{ Torr}) V_2 + 72.037 \text{ Torr dm}^3$$

Now the above can be simplified on both sides to obtain,

$$102.91 \text{ Torr dm}^3 = (286.9896 \text{ Torr}) V_2$$

$$V_2 = V_{\text{manifold}} = \frac{102.91 \cancel{\text{Torr}} \text{ dm}^3}{286.9896 \cancel{\text{Torr}}}$$

$$\boxed{V_{\text{manifold}} = 0.359 \text{ dm}^3}$$

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**1.11.** An ideal gas occupies a volume of  $0.300 \text{ dm}^3$  at a pressure of  $1.80 \times 10^5 \text{ Pa}$ . What is the new volume of the gas maintained at the same temperature if the pressure is reduced to  $1.15 \times 10^5 \text{ Pa}$ ?

**Solution:**

Given: Ideal Gas:  $V_1 = 0.300 \text{ dm}^3$ ,  $P_1 = 1.80 \times 10^5 \text{ Pa}$

Required:  $V_2$

In this particular situation, Boyle's Law will apply. This law describes the product of pressure and volume for a closed system. In a closed system, the temperature and moles are constant, thus;

$$P_1 V_1 = P_2 V_2$$

Simply rearrange for the final volume ( $V_2$ );

$$V_2 = \frac{P_1 V_1}{P_2}$$

$$V_2 = \frac{(1.80 \times 10^5 \text{ Pa})(0.300 \text{ dm}^3)}{(1.15 \times 10^5 \text{ Pa})}$$

$$\boxed{V_2 = 0.470 \text{ dm}^3}$$

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**1.12.** If the gas in Problem 1.11 were initially at 330 K, what will be the final volume if the temperature were raised to 550 K at constant pressure?

**Solution:**

Given: same gas as in problem 1.11:  $V_1 = 0.300 \text{ dm}^3$

$$T_1 = 330 \text{ K}, T_2 = 550 \text{ K} \text{ (constant pressure)}$$

Required:  $V_2$

In this particular situation, Charles' Law will apply. This law states that under constant pressure, the volume of an ideal gas will vary proportionately (by the same factor) with changes in temperature, thus;

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Simply rearrange for the final volume ( $V_2$ );

$$V_2 = \frac{V_1 T_2}{T_1}$$

$$V_2 = \frac{(0.300 \text{ dm}^3)(550 \text{ K})}{330 \text{ K}}$$

$$\boxed{V_2 = 0.500 \text{ dm}^3}$$

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**1.13.** Calculate the concentration in  $\text{mol dm}^{-3}$  of an ideal gas at 298.15 K and at (a) 101.325 kPa (1 atm), and (b)  $1.00 \times 10^{-4}$  Pa ( $= 10^{-9}$  atm). In each case, determine the number of molecules in  $1.00 \text{ dm}^3$ .

**Solution:**

Given: Ideal Gas:  $T = 298.15 \text{ K}$ ,  $P_1 = 101.325 \text{ kPa}$  (1 atm),  $P_2 = 1.00 \times 10^{-4} \text{ Pa}$  ( $10^{-9} \text{ atm}$ )

Required:  $C$  (in  $\text{mol dm}^{-3}$ )

$N_A$  (in  $V = 1.00 \text{ dm}^3$ )

Knowing that concentration is equal to:

$$C = \frac{n}{V}$$

we can make the substitution into the Ideal Gas Law.

$$C = \frac{n}{V} = \frac{P}{RT}$$

For pressure (a) and using the fact that  $\text{m}^3 = \text{J Pa}^{-1}$ :

$$C_1 = \frac{n}{V} = \frac{P_1}{RT}$$

$$C_1 = \frac{1.01325 \times 10^5 \text{ Pa}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$C_1 = 40.87 \text{ mol m}^{-3}$$

Now convert units into  $\text{mol dm}^{-3}$ :

$$C_1 = \frac{40.87 \text{ mol m}^{-3}}{10^3} = 0.0409 \text{ mol dm}^{-3}$$

$$C_1 = 0.0409 \text{ mol dm}^{-3}$$

Number of molecules per unit volume;

$$(0.0409 \text{ mol dm}^{-3})(L) = (0.0409 \cancel{\text{mol}} \text{ dm}^{-3}) \left( 6.022 \times 10^{23} \text{ molecules } \cancel{\text{mol}^{-1}} \right)$$

$$N_1 = \frac{2.46 \times 10^{22} \text{ molecules } \cancel{\text{dm}^3}}{1.00 \cancel{\text{dm}^3}} = 2.46 \times 10^{22} \text{ molecules}$$

$$N_1 = 2.46 \times 10^{22} \text{ molecules}$$

For pressure (b) using the same method:

$$C_2 = \frac{n}{V} = \frac{P_2}{RT}$$

$$C_2 = \frac{1.00 \times 10^{-4} \text{ Pa}}{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1})(298.15 \cancel{\text{K}})}$$

$$C_2 = 4.03 \times 10^{-8} \text{ mol m}^{-3}$$

Now convert units into  $\text{mol dm}^{-3}$ ;

$$C_2 = \frac{4.03 \times 10^{-8} \text{ mol m}^{-3}}{10^3} = 4.03 \times 10^{-11} \text{ mol dm}^{-3}$$

$$C_2 = 4.03 \times 10^{-11} \text{ mol dm}^{-3}$$

Number of molecules per unit volume;

$$(4.03 \times 10^{-11} \text{ mol dm}^{-3})(L) = (4.03 \times 10^{-11} \cancel{\text{mol}} \text{ dm}^{-3}) \left( 6.022 \times 10^{23} \text{ molecules } \cancel{\text{mol}^{-1}} \right)$$



$$N_2 = \frac{2.43 \times 10^{13} \text{ molecules } \cancel{\text{dm}^3}}{1.00 \cancel{\text{dm}^3}} = 2.43 \times 10^{13} \text{ molecules}$$

$$N_2 = 2.43 \times 10^{13} \text{ molecules}$$

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- 1.14.** A J-shaped tube is filled with air at 760 Torr and 22 °C. The long arm is closed off at the top and is 100.0 cm long; the short arm is 40.00 cm high. Mercury is poured through a funnel into the open end. When the mercury spills over the top of the short arm, what is the pressure on the trapped air? Let  $h$  be the length of mercury in the long arm.

**Solution:**

Given: J-Tube:  $P = 760$  Torr,  $T = 22$  °C, long arm  $h = 100$  cm, short arm  $l = 40$  cm

Required:  $P$  of trapped air

The temperature is again held constant (same as in problems 1.10 and 1.11) so Boyle's Law will apply;

$$P_1V_1 = P_2V_2$$

We are given the initial pressure, so we can rearrange this equation to solve for  $P_2$ ;

$$P_2 = \frac{P_1V_1}{V_2}$$

Since  $h$ , the height of the mercury column on the trapped air side (long arm) is proportional to the volume of a uniform tube then we can write;

$$P_2 = \frac{P_1 \times 100 \text{ cmHg}}{(100 - h) \text{ cmHg}}$$

where  $h$  is the final height in centimeters of mercury in the long arm. In the short arm;

$$P_2 = 40 - h + P_1$$

Substituting this into the above equation in order to eliminate  $P_2$  gives;

$$40 - h + P_1 = \frac{P_1 \times 100 \text{ cmHg}}{(100 - h) \text{ cmHg}}$$

Recall that 1mmHg = 1 Torr and we therefore can make the substitution for  $P_1$ ;

$$\frac{P_1(100)}{(100-h)} = 40 - h + P_1$$

$$P_1(100) = (100-h)(40-h+P_1)$$

This can be expanded to obtain;

$$\cancel{P_1(100)} = 4000 - 100h + \cancel{100P_1} - 40h + h^2 - P_1h$$

$$h^2 - 140h - 76h + 4000 = 0$$

$$h^2 - 216h + 4000 = 0$$

Using the quadratic equation then yields:

$$\boxed{h = 195.5 \text{ cmHg}} \text{ or } \boxed{h = 20.5 \text{ cmHg}}$$

The first value of  $h$  cannot be this large since the tube length is only 100 cm. Therefore,

$$\boxed{h = 20.5 \text{ cmHg}} \text{ is the correct value.}$$

The final pressure can now be found;

$$P_2 = \frac{P_1(100)}{(100-h)} \rightarrow \frac{76 \text{ cmHg}(100\cancel{\text{cm}})}{(100-20.5)\cancel{\text{cm}}} = 95.6 \text{ cmHg}$$

$$\boxed{P_2 = 956 \text{ Torr}}$$

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**1.15.** A Dumas experiment to determine molar mass is conducted in which a gas sample's  $P$ ,  $\theta$ , and  $V$  are determined. If a 1.08-g sample is held in  $0.250 \text{ dm}^3$  at  $303 \text{ K}$  and  $101.3 \text{ kPa}$ :

- What would the sample's volume be at  $273.15 \text{ K}$ , at constant pressure?
- What is the molar mass of the sample?

**Solution:**

Given:  $m = 1.08 \text{ g}$ ,  $V = 0.250 \text{ dm}^3$ ,  $T = 303 \text{ K}$ ,  $P = 101.3 \text{ kPa}$

Required:  $V_{\text{sample}}$  and  $M_{\text{sample}}$

Since we are working under constant pressure, Charles' Law can be applied. This law states that

$$\frac{V_1}{T_1} = \text{constant} = \frac{V_2}{T_2}$$

Solving for  $V_2$ , we obtain

$$V_2 = \frac{V_1 T_2}{T_1}$$

Remember that the initial temperature is  $T = 303 \text{ K}$  so by making the appropriate substitutions we will have;

$$V_2 = \frac{(0.250 \text{ dm}^3)(273.15 \cancel{\text{K}})}{303 \cancel{\text{K}}}$$

$$\boxed{V_2 = 0.225 \text{ dm}^3}$$

Now that we have the final volume, it is possible to find the molar mass according to the equation;

$$M = \frac{mRT}{PV}$$

Recall that in order to derive this equation we must start with the ideal gas law;

$PV = nRT$  and  $n = \frac{m}{M}$  so we obtain

$$PV = \frac{m}{M}RT \rightarrow M = \frac{mRT}{PV}$$

$$M = \frac{(1.08 \times 10^{-3} \text{ kg})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{(101.3 \times 10^3 \text{ Pa})(0.225 \text{ dm}^3)(10^{-3} \text{ m}^3 \text{ dm}^{-3})}$$

$$M = 0.1076 \text{ kg mol}^{-1} \rightarrow \boxed{M = 108 \text{ g mol}^{-1}}$$

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**1.16.** A gas that behaves ideally has a density of  $1.92 \text{ g dm}^{-3}$  at 150 kPa and 298 K. What is the molar mass of the sample?

**Solution:**

Given: Ideal Gas:  $\rho = 1.92 \text{ g dm}^{-3}$ ,  $P = 150 \text{ kPa}$ ,  $T = 298 \text{ K}$

Required:  $M_{\text{sample}}$

Starting with the Ideal Gas Law is it possible to make substitutions and rearrangements in order to solve for the molar mass.

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

Now, using the fact that  $n = \frac{m}{M}$  we can make the next substitution;

$$P = \frac{\frac{m}{M} RT}{V}$$

Since density is defined as  $\rho = \frac{m}{V}$  then we can write;

$$P = \frac{\rho RT}{M} \text{ and now solve for } M \rightarrow M = \frac{\rho RT}{P}$$

$$M = \frac{\rho RT}{P} = \frac{1.92 \text{ kg m}^{-3} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{150 \times 10^3 \text{ Pa}}$$

$$M = 0.0317 \text{ kg mol}^{-1}$$

$$\boxed{M = 31.7 \text{ g mol}^{-1}}$$

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**1.17.** The density of air at 101.325 kPa and 298.15 K is  $1.159 \text{ g dm}^{-3}$ . Assuming that air behaves as an ideal gas, calculate its molar mass.

**Solution:**

Given: Air:  $\rho = 1.159 \text{ g dm}^{-3}$ ,  $T = 298.15 \text{ K}$ ,  $P = 101.325 \text{ kPa}$

Required:  $M_{\text{air}}$

Use the same method as the previous problem (1.16);

$$M = \frac{\rho RT}{P}$$

$$M = \frac{\rho RT}{P} = \frac{1.159 \text{ kg m}^{-3} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{101\,325 \text{ Pa}}$$

$$M = 0.0284 \text{ kg mol}^{-1}$$

$$\boxed{M = 28.36 \text{ g mol}^{-1}}$$

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**1.18.** A  $0.200\text{-dm}^3$  sample of  $\text{H}_2$  is collected over water at a temperature of  $298.15\text{ K}$  and at a pressure of  $99.99\text{ kPa}$ . What is the pressure of hydrogen in the dry state at  $298.15\text{ K}$ ? The vapor pressure of water at  $298.15\text{ K}$  is  $3.17\text{ kPa}$ .

**Solution:**

Given:  $\text{H}_2$  (over water):  $V = 0.200\text{ dm}^3$ ,  $T = 298.15\text{ K}$ ,  $P_t = 99.99\text{ kPa}$

Vapor pressure of water:  $3.17\text{ kPa}$  at  $T = 298.15\text{ K}$

Required:  $P_{\text{H}_2}$  in the dry state

This problem makes use of Dalton's Law of Partial Pressures which states:

The total pressure observed for a mixture of gases is equal to the sum of the pressure that each individual gas would exert had it been alone occupying the container and at the same temperature.

$$P_i = x_i P_t$$

Partial pressure is defined as the total pressure multiplied by the mole fraction of a particular gas in the mixture. For this particular hydrogen/water system, we can then write;

$$P_t = P_{\text{H}_2} + P_{\text{H}_2\text{O}} \text{ and solve for the pressure of hydrogen;}$$

$$P_t - P_{\text{H}_2\text{O}} = P_{\text{H}_2}$$

$$P_{\text{H}_2} = 99.99\text{ kPa} - 3.17\text{ kPa}$$

$$\boxed{P_{\text{H}_2} = 96.82\text{ kPa}}$$

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**1.19.** What are the mole fractions and partial pressures of each gas in a 2.50-L container into which 100.00 g of nitrogen and 100.00 g of carbon dioxide are added at 25 °C? What is the total pressure?

**Solution:**

Given: Container:  $V = 2.50 \text{ L}$ ,  $T = 25 \text{ °C}$

Add 100.00 g of nitrogen and carbon dioxide

Required:  $x_i$ ,  $P_i$  for each and  $P_t$

First find the amount of each gas in terms of moles because we are provided with their mass and can easily find their molar mass;

$$n_{\text{N}_2} = \frac{m}{M} \rightarrow \frac{100.00 \cancel{\text{g}}}{28.012 \cancel{\text{g}} \text{ mol}^{-1}}$$

$$n_{\text{N}_2} = 3.5699 \text{ mol}$$

$$n_{\text{CO}_2} = \frac{m}{M} \rightarrow \frac{100.00 \cancel{\text{g}}}{44.010 \cancel{\text{g}} \text{ mol}^{-1}}$$

$$n_{\text{CO}_2} = 2.2722 \text{ mol}$$

Now we can find the mole fractions associated with each gas using the individual and combined number of moles;

$$x_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{tot}}} \rightarrow \frac{3.5699 \cancel{\text{mol}}}{(3.5699 + 2.2722) \cancel{\text{mol}}}$$

$$\boxed{x_{\text{N}_2} = 0.6111}$$

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{tot}}} \rightarrow \frac{2.2722 \cancel{\text{mol}}}{(3.5699 + 2.2722) \cancel{\text{mol}}}$$

$$\boxed{x_{\text{CO}_2} = 0.3889}$$

Knowing the container volume and temperature of the system, the partial pressures can be calculated using the ideal gas law;

$$P_{N_2} = \frac{n_{N_2} RT}{V_{\text{cont}}} \rightarrow \frac{(3.5699 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{2.50 \text{ dm}^3}$$

$$\boxed{P_{N_2} = 35.4 \text{ bar}}$$

$$P_{CO_2} = \frac{n_{CO_2} RT}{V_{\text{cont}}} \rightarrow \frac{(2.2722 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{2.50 \text{ dm}^3}$$

$$\boxed{P_{CO_2} = 22.5 \text{ bar}}$$

The total pressure is now found using Dalton's Law for Partial Pressures;

$$P_t = P_1 + P_2 + P_3 + \dots + P_i$$

$$P_t = x_1 P_t + x_2 P_t + x_3 P_t + \dots + x_i P_t \quad (\text{Eq. 1.53})$$

$$P_t = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \dots + \frac{n_i RT}{V}$$

$$P_t = (n_1 + n_2 + \dots + n_i) \frac{RT}{V} \quad (\text{Eq. 1.54})$$

Any of the above forms can be used but for simplicity, we shall use Eq. 1.54;

$$P_t = (3.5699 + 2.2722) \text{ mol} \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{2.50 \text{ dm}^3}$$

$$\boxed{P_t = 57.9 \text{ bar}}$$

Notice, once you take the pressure, you need to divide by  $10^2$  in order to get the pressure in units bar.

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**1.20.** The decomposition of  $\text{KClO}_3$  produces  $27.8 \text{ cm}^3$  of  $\text{O}_2$  collected over water at  $27.5^\circ\text{C}$ . The vapor pressure of water at this temperature is 27.5 Torr. If the barometer reads 751.4 Torr, find the volume the dry gas would occupy at  $25.0^\circ\text{C}$  and 1.00 bar.

**Solution:**

Given:  $\text{KClO}_3$ :  $V_{\text{O}_2} = 27.8 \text{ cm}^3$ ,  $T = 27.5^\circ\text{C}$

Vapor pressure of water:  $P = 27.5 \text{ Torr}$

Barometer reading:  $P = 751.4 \text{ Torr}$

Required:  $V_{\text{dry gas}}$

First it is possible to find the pressure of the dry gas at  $T = 27.5^\circ\text{C}$  by making use of the barometer reading and the vapor pressure of water;

$$P_{\text{gas}} = P_{\text{barometer}} - P_{\text{water}}$$

$$P_{\text{gas}} = 751.4 \text{ Torr} - 27.5 \text{ Torr}$$

$$P_{\text{gas}} = 723.9 \text{ Torr (Remember that this is at } 27.5^\circ\text{C)}$$

Since there is also a temperature change the following equality should be used to find the final volume of the system;

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

Recall that 1 bar = 750.06 Torr. Also, when making temperature conversions between Celsius to Kelvin:  $27.5^\circ\text{C} = 273.15 + 27.5 = 300.65 \text{ K}$ .

It is important to remember the initial conditions of the system (Don't mix up the temperatures!);

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} \rightarrow \frac{(723.9 \cancel{\text{Torr}})(27.8 \text{ cm}^3)(298.15 \cancel{\text{K}})}{(300.65 \cancel{\text{K}})(750.06 \cancel{\text{Torr}})}$$

$$V_2 = V_{\text{dry gas}} = 26.6 \text{ cm}^3$$

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**1.21.** Balloons now are used to move huge trees from their cutting place on mountain slopes to conventional transportation. Calculate the volume of a balloon needed if it is desired to have a lifting force of 1000 kg when the temperature is 290 K at 0.940 atm. The balloon is to be filled with helium. Assume that air is 80 mol %  $N_2$  and 20 mol %  $O_2$ . Ignore the mass of the superstructure and propulsion engines of the balloon.

**Solution:**

Given: Balloon lifting force:  $m = 1000 \text{ kg}$ ,  $T = 290 \text{ K}$ ,  $P = 0.940 \text{ atm}$

Required:  $V_{\text{balloon}}$

The lifting force comes from the difference between the mass of air displaced and the mass of the helium that replaces the air. We can work under the assumption that the molar mass for air is  $28.8 \text{ g mol}^{-1}$ . This is true if we consider the fact that air (in the problem) is composed 80 percent of nitrogen and 20 percent of oxygen.

$$M_{N_2} \approx 14(2) = 28 \text{ g mol}^{-1}$$

But we will only consider 80 percent and therefore;

$$M_{N_2} = 28 \text{ g mol}^{-1}(0.80) = 22.4 \text{ g mol}^{-1} \text{ (in air)}$$

$$M_{O_2} \approx 16(2) = 32 \text{ g mol}^{-1}$$

But we will only consider 20 percent and therefore;

$$M_{O_2} = 32 \text{ g mol}^{-1}(0.20) = 6.4 \text{ g mol}^{-1}$$

$$\text{Lifting force} \rightarrow V(\rho_{\text{air}} - \rho_{\text{helium}}) = 1000 \text{ kg}$$

And recall that we can use the ideal gas law to solve for the density of a gas (density is mass divided by volume);

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{\frac{m}{M}RT}{V} = \frac{\rho}{M}RT \text{ and solve for density}$$

$$\rho = \frac{PM}{RT}$$

$$\rho_{\text{air}} = \frac{(0.940 \cancel{\text{atm}})(101325 \text{ Pa} \cancel{\text{atm}^{-1}})(28.8 \cancel{\text{g}} \cancel{\text{mol}^{-1}})}{(8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}})(290 \cancel{\text{K}})(10^3 \cancel{\text{g}} \text{ kg}^{-1})}$$

$$\rho_{\text{air}} = 1.138 \text{ kg m}^{-3}$$

$$\rho_{\text{helium}} = \frac{(0.940 \cancel{\text{atm}})(101325 \text{ Pa} \cancel{\text{atm}^{-1}})(4.003 \cancel{\text{g}} \cancel{\text{mol}^{-1}})}{(8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}})(290 \cancel{\text{K}})(10^3 \cancel{\text{g}} \text{ kg}^{-1})}$$

$$\rho_{\text{helium}} = 0.158 \text{ kg m}^{-3}$$

Now these values can be substituted into the equation for the volume of the balloon;

$$V_{\text{balloon}} = \frac{1000 \text{ kg}}{(\rho_{\text{air}} - \rho_{\text{helium}})}$$

$$V_{\text{balloon}} = \frac{1000 \cancel{\text{kg}}}{(1.138 - 0.158) \cancel{\text{kg}} \text{ m}^{-3}}$$

$$\boxed{V_{\text{balloon}} = 1021 \text{ m}^3}$$

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**1.22.** A gas mixture containing 5 mol % butane and 95 mol % argon (such as is used in Geiger-Müller counter tubes) is to be prepared by allowing gaseous butane to fill an evacuated cylinder at 1 atm pressure. The 40.0-dm<sup>3</sup> cylinder is then weighed. Calculate the mass of argon that gives the desired composition if the temperature is maintained at 25.0 °C. Calculate the total pressure of the final mixture. The molar mass of argon is 39.9 g mol<sup>-1</sup>.

**Solution:**

Given: Gas mixture: 5 mol % butane and 95 mol % argon

$$P = 1 \text{ atm}, V_{\text{cyl}} = 40.0 \text{ dm}^3, M_{\text{argon}} = 39.9 \text{ g mol}^{-1}$$

Required:  $m_{\text{argon}}$  and  $P_t$

By using the information given above, it is possible to find the mole fractions for each of the gases in the mixture;

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n_{\text{butane}} = \frac{(101325 \text{ Pa})(40.0 \text{ dm}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$n_{\text{butane}} = 1.63 \text{ mol}$$

Since the mixture contains 95 parts argon to 5 parts of butane, the ratio is then 95/5 = 19:1 and we can determine the number of moles for argon;

$$n_{\text{argon}} = 19 n_{\text{butane}}$$

$$n_{\text{argon}} = 19(1.63) \text{ mol} = 30.97 \text{ mol}$$

Now that we have both the number of moles and molar mass, we can find the mass of argon;

$$m_{\text{argon}} = n_{\text{argon}} M_{\text{argon}}$$

$$m_{\text{argon}} = (30.97 \cancel{\text{mol}}) (39.9 \text{ g } \cancel{\text{mol}^{-1}})$$

$$m_{\text{argon}} = 1236.7 \text{ g}$$

The total pressure can then be found by taking the sum of the partial pressures;

$$P_t = (n_{\text{butane}} + n_{\text{argon}}) \frac{RT}{V}$$

Remember that once you find the pressure, you must divide by  $10^2$  in order to convert to bar.

$$P_t = (1.63 + 30.97) \cancel{\text{mol}} \frac{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}}) (298.15 \text{ K})}{40.0 \text{ dm}^3}$$

$$P_t = 20.2 \text{ bar}$$

Since  $1 \text{ bar} = 0.986 92 \text{ atm}$ , then we can say that;

$$P_t = 20.2(0.986 92)$$

$$P_t = 19.9 \text{ atm}$$

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**1.23.** The gravitational constant  $g$  decreases by  $0.010 \text{ m s}^{-2} \text{ km}^{-1}$  of altitude.

**a.** Modify the barometric equation to take this variation into account. Assume that the temperature remains constant.

**b.** Calculate the pressure of nitrogen at an altitude of 100 km assuming that sea-level pressure is exactly 1 atm and that the temperature of 298.15 K is constant.

**Solution:**

Given: gravitational constant  $g$  decreases by  $0.010 \text{ m s}^{-2} \text{ km}^{-1}$  of altitude

Required: (a) modify  $\frac{dP}{P} = -\left(\frac{Mg}{RT}\right) dz$

(b)  $P_{\text{N}_2}$  at  $z = 100 \text{ km}$ ,  $P = 1 \text{ atm}$ ,  $T = 298.15 \text{ K}$

**a)** The standard gravitational acceleration is defined as  $9.807 \text{ m s}^{-2}$ . If  $g$  were to decrease by  $0.010 \text{ m s}^{-2}$  per each kilometer in height, this would be equivalent to a change of:

$$\frac{0.010 \cancel{\text{m}} \text{s}^{-2}}{10^3 \cancel{\text{m}}} = 10^{-5} \text{ s}^{-2} z$$

where  $z$  is the altitude. The new gravitational constant expression would be as follows:

$$g = 9.807 \text{ m s}^{-2} - 10^{-5} \text{ s}^{-2} z$$

This can then be substituted into the Barometric Distribution Law equation,

$$\frac{dP}{P} = -\left(\frac{Mg}{RT}\right) dz \quad (\text{Eq. 1.74})$$

To give:

$$\boxed{\frac{dP}{P} = -\frac{M}{RT} (9.807 \text{ m s}^{-2} - 10^{-5} \text{ s}^{-2} z) dz}$$

This can also be expressed in the following manner:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{M}{RT}\left(9.807 \text{ m s}^{-2} z - 5 \times 10^{-6} \text{ s}^{-2} z^2\right)$$

b) The second version of this equation can then be used to calculate the pressure of nitrogen gas at an altitude of 100 km.

$$\ln\left(\frac{P}{P_0}\right) = -\frac{\left(28.0 \cancel{\text{g mol}^{-1}}\right)\left(10^{-3} \cancel{\text{kg g}^{-1}}\right)}{\left(8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}}\right)(298.15 \text{ K})}\left(9.807(10^5) \text{ m s}^{-2} z - 5 \times 10^{-6} (10^5)^2 \text{ s}^{-2} z^2\right)$$

$$\ln\left(\frac{P}{P_0}\right) = -10.51$$

$$\left(\frac{P}{P_0}\right) = e^{-10.51} = 2.73 \times 10^{-5}$$

$$P = 2.73 \times 10^{-5} (P_0 = 1 \text{ atm})$$

$$\boxed{P = 2.73 \times 10^{-5} \text{ atm}}$$

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- 1.24.** Suppose that on another planet where the atmosphere is ammonia that the pressure on the surface, at  $h = 0$ , is 400 Torr at 250 K. Calculate the pressure of ammonia at a height of 8000 metres. The planet has the same  $g$  value as the earth.

**Solution:**

Given: Planet with ammonia atmosphere:  $h = 0$ ,  $P = 400$  Torr,  $T = 250$  K

Required:  $P_{\text{NH}_3}$  at  $h = 8000$  m

We may begin as we did in the previous problem with the Barometric Distribution Law:

$$\frac{dP}{P} = -\left(\frac{Mg}{RT}\right) dz \quad (\text{Eq. 1.74})$$

We can then integrate this expression, with the boundary condition that  $P = P_0$  when  $z = 0$ , which yields;

$$\ln \frac{P}{P_0} = -\frac{Mgz}{RT} \quad (\text{Eq. 1.75})$$

We can further manipulate the equation by exponentiating each side:

$$\cancel{\ln e} \frac{P}{P_0} = e^{-\frac{Mgz}{RT}} \text{ and solve for } P$$

$$P = P_0 e^{-\frac{Mgz}{RT}}$$

Assume that the temperature remains constant at  $T = 250$  K and the molar mass of ammonia is  $M = 0.017$  kg mol<sup>-1</sup>. These values can be substituted into the above equation.

$$P = (400 \text{ Torr}) e^{\frac{(-0.017)(9.807)(8000)}{(8.3145)(250)}}$$

$$P = (400 \text{ Torr}) e^{-0.642}$$

$$\boxed{P = 210 \text{ Torr}}$$

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**1.25.** Pilots are well aware that in the lower part of the atmosphere the temperature decreases linearly with altitude. This dependency may be written as  $T = T_0 - az$ , where  $a$  is a proportionality constant,  $z$  is the altitude, and  $T_0$  and  $T$  are the temperatures at ground level and at altitude  $z$ , respectively. Derive an expression for the barometric equation that takes this into account. Work to a form involving  $\ln(P/P_0)$ .

**Solution:**

Given: linear dependency of temperature on altitude:  $T = T_0 - az$

Required: Derive an expression for the barometric equation taking linearity of temperature increase into account.

Beginning with the Barometric Distribution Law equation (Eq. 1.74), and substituting for  $T$  from the linear dependency of temperature on altitude equation;

$$\frac{dP}{P} = - \left( \frac{Mg}{RT} \right) dz$$

$$\frac{dP}{P} = - \frac{Mg}{R(T_0 - az)} dz$$

This is a differential equation. In order to solve this, let  $x = (T_0 - az)$  then we have:

$$dx = -adz \text{ and rearrangement gives } \rightarrow dz = \frac{-dx}{a}$$

Integration of the expression is then as follows (and with the proper substitutions):

$$\int_{x_0}^x \frac{-dx}{ax} = \frac{-1}{a} \ln \left( \frac{x}{x_0} \right)$$

$$\int_{x_0}^x \frac{-dx}{ax} = \frac{1}{a} \ln \left( \frac{T_0}{T_0 - az} \right)$$

Integration of the LHS between the values  $P_0$  and  $P$  (with the final substitution) gives:

$$\ln\left(\frac{P}{P_0}\right) = \frac{Mg}{Ra} \ln\left(\frac{T_0 - az}{T_0}\right)$$

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- 1.26.** An ideal gas thermometer and a mercury thermometer are calibrated at 0 °C and at 100 °C. The thermal expansion coefficient for mercury is:

$$\alpha = \frac{1}{V_0} (\partial V / \partial T)_p$$

$$= 1.817 \times 10^{-4} + 5.90 \times 10^{-9} \theta + 3.45 \times 10^{-10} \theta^2$$

where  $\theta$  is the value of the Celsius temperature and  $V_0 = V$  at  $\theta = 0$ . What temperature would appear on the mercury scale when the ideal gas scale reads 50 °C?

**Solution:**

Given: Thermometers:  $T_1 = 0$  °C,  $T_2 = 100$  °C

Thermal expansion coefficient for mercury:  $\alpha = \frac{1}{V_0} (\partial V / \partial T)_p = 1.817 \times 10^{-4} + 5.90 \times 10^{-9} \theta + 3.45 \times 10^{-10} \theta^2$

Required:  $\theta_{\text{Hg}}$  when ideal gas scale reads 50 °C

In the case of a mercury column, we assign its length the value  $l_{100}$  when it is at thermal equilibrium with boiling water vapor at 1 atm pressure. The achievement of equilibrium with melting ice exposed to 1 atm pressure establishes the length,  $l_0$ . Assuming a linear relationship between the temperature and the thermometric property (length) we can write;

$$\theta = \frac{(l - l_0)}{(l_{100} - l_0)} (100 \text{ °C}) \quad (\text{Eq. 1.15})$$

This expression can be tailored to the situation given above by;

$$\theta_{\text{Hg}} = \frac{(V_{50} - V_0)_{\text{Hg}}}{(V_{100} - V_0)_{\text{Hg}}} (100 \text{ °C})$$

Since  $\alpha = \frac{1}{V_0} (\partial V / \partial T)_p$  then we can integrate the expression with respect to  $\alpha$  to get;

$$V_{50} - V_0 = \int_0^{50} \alpha V_0 d\theta$$

which can be evaluated as follows (divide the second and third terms by 2 and 3 respectively)

$$\begin{aligned} & \left[ 1.817 \times 10^{-4} \theta \Big|_0^{50} + 2.95 \times 10^{-9} \theta^2 \Big|_0^{50} + 1.15 \times 10^{-10} \theta^3 \Big|_0^{50} \right] V_0 \\ &= 0.009\,107\,V_0 \end{aligned}$$

The same can be done for the denominator in the equation  $\theta_{\text{Hg}} = \frac{(V_{50} - V_0)_{\text{Hg}}}{(V_{100} - V_0)_{\text{Hg}}} (100\,^{\circ}\text{C})$

$$\begin{aligned} & \left[ 1.817 \times 10^{-4} \theta \Big|_0^{100} + 2.95 \times 10^{-9} \theta^2 \Big|_0^{100} + 1.15 \times 10^{-10} \theta^3 \Big|_0^{100} \right] V_0 \\ &= 0.018\,31\,V_0 \end{aligned}$$

Now these two values can be substituted into the above equation to get;

$$\theta_{\text{Hg}} = \frac{0.009\,107\,V_0}{0.018\,31\,V_0} (100\,^{\circ}\text{C})$$

$$\boxed{\theta_{\text{Hg}} = 49.7\,^{\circ}\text{C}}$$

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**1.27.** It takes gas A 2.3 times as long to effuse through an orifice as the same amount of nitrogen. What is the molar mass of gas A?

**Solution:**

Given: Gas A:  $t_{\text{effusion}} = 2.3$  times longer than nitrogen

Required:  $M_{\text{Gas A}}$

This particular problem makes use of Graham's Law of Effusion which states that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles:

$$\frac{\text{rate}(\text{gas 1})}{\text{rate}(\text{gas 2})} = \frac{t(\text{gas 2})}{t(\text{gas 1})} = \sqrt{\frac{\rho(\text{gas 2})}{\rho(\text{gas 1})}} = \sqrt{\frac{M(\text{gas 2})}{M(\text{gas 1})}}$$

Since we can easily determine the molar mass of nitrogen ( $\text{N}_2$ ), we can make the appropriate substitutions and solve for the molar mass of Gas A.

$$M_{\text{nitrogen}} = 28 \text{ g mol}^{-1}$$

$$\frac{v_A}{v_{\text{nitrogen}}} = \frac{t_{\text{nitrogen}}}{t_A} = \sqrt{\frac{M(\text{gas 2})}{M(\text{gas 1})}}$$

$$\frac{v_A}{v_{\text{nitrogen}}} = \frac{1}{2.3} = \sqrt{\frac{28 \text{ g mol}^{-1}}{M_A}} \rightarrow \left(\frac{1}{2.3}\right)^2 = \left(\sqrt{\frac{28 \text{ g mol}^{-1}}{M_A}}\right)^2$$

$$\left(\frac{1}{2.3}\right)^2 = \frac{28 \text{ g mol}^{-1}}{M_A} \rightarrow M_A = \frac{28 \text{ g mol}^{-1}}{\left(\frac{1}{2.3}\right)^2}$$

$$M_A = 1.5 \times 10^2 \text{ g mol}^{-1}$$

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**1.28.** Exactly  $1 \text{ dm}^3$  of nitrogen, under a pressure of 1 bar, takes 5.80 minutes to effuse through an orifice. How long will it take for helium to effuse under the same conditions?

**Solution:**

Given:  $V_{\text{nitrogen}} = 1 \text{ dm}^3$ ,  $P = 1 \text{ bar}$ ,  $t = 5.8 \text{ min}$

Required:  $t_{\text{He}}$

Using Graham's Law of effusion (as in previous problem 1.27) recall that effusion time is inversely proportional to the *rate* of effusion.

$$\frac{\text{rate}(\text{N}_2)}{\text{rate}(\text{He})} = \frac{t_{\text{He}}}{t_{\text{N}_2}} = \sqrt{\frac{M_{\text{He}}}{M_{\text{N}_2}}}$$

Rearrange the above equation to isolate for the wanted variable,  $t_{\text{He}}$ ;

$$t_{\text{He}} = t_{\text{N}_2} \sqrt{\frac{M_{\text{He}}}{M_{\text{N}_2}}}$$

We can determine the molar masses of both helium and nitrogen to get;

$$t_{\text{He}} = 5.80 \text{ min} \sqrt{\frac{4 \text{ g mol}^{-1}}{28 \text{ g mol}^{-1}}}$$

$$t_{\text{He}} = 2.19 \text{ min}$$

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**1.29.** What is the total kinetic energy of 0.50 mol of an ideal monatomic gas confined to 8.0 dm<sup>3</sup> at 200 kPa?

**Solution:**

Given: Ideal monatomic gas:  $n = 0.50$  mol,  $V = 8.0$  dm<sup>3</sup>,  $P = 200$  kPa

Required:  $E_{k_{\text{tot}}}$

This particular problem refers to the section of *Kinetic Theory of Gases*. Here, we are trying to determine the relationship between  $\overline{u^2}$  and  $T$ , the mechanical variable of  $u$  of Eq. 1.41:

$$P = \frac{Nm\overline{u^2}}{3V}$$

which is the fundamental equation derived from the simple kinetic theory of gases. For our purpose of determining this relationship (kinetic energy and temperature), Eq. 1.41 may be converted into another useful form by recognizing that the average kinetic energy per molecule is defined as;

$$\overline{\epsilon_k} = \frac{1}{2}m\overline{u^2}$$

Substitution of this expression into Eq. 1.41 then gives;

$$PV = \frac{1}{3}N \cdot 2\overline{\epsilon_k} = \frac{2}{3}N\overline{\epsilon_k}$$

At constant pressure, the volume of a gas is proportional to the number of molecules and the average kinetic energy of the molecules. Since  $N = nL$  then we can write;

$$PV = \frac{2}{3}nL\overline{\epsilon_k} \text{ and since } L\overline{\epsilon_k} \text{ is the total kinetic energy per mole of gas, then}$$

$$PV = \frac{2}{3}nE_k$$

$$E_k = \frac{3}{2} \frac{PV}{n}$$

The data given above can be substituted into the above equation to yield;

$$E_k = \frac{3}{2} \frac{(200 \text{ kPa})(8.0 \text{ dm}^3)}{0.5 \text{ mol}}$$

$$E_k = 4800 \text{ J mol}^{-1}$$

So for half a mole, the kinetic energy will be:

$$nE_k = 2400 \text{ J}$$

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**1.30.** Nitrogen gas is maintained at 152 kPa in a 2.00-dm<sup>3</sup> vessel at 298.15 K. If its molar mass is 28.0134 g mol<sup>-1</sup> calculate:

- The amount of N<sub>2</sub> present.
- The number of molecules present.
- The root-mean-square speed of the molecules.
- The average translational kinetic energy of each molecule.
- The total translational kinetic energy in the system.

**Solution:**

Given: Nitrogen:  $P = 152 \text{ kPa}$ ,  $V = 2.00 \text{ dm}^3$ ,  $T = 298.15 \text{ K}$ ,  $M = 28.0134 \text{ g mol}^{-1}$

Required: see above **a** through **e**

Using the ideal gas law,  $PV = nRT$  we can solve for the number of moles present.

$$n = \frac{PV}{RT} \rightarrow \frac{(152\,000 \text{ Pa})(2.00 \text{ dm}^3)(10^{-3} \text{ m}^3 \text{ dm}^{-3})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$\boxed{n = 0.1226 \text{ mol}}$$

We can now use Avogadro's number in order to find the number of molecules present;

$$\text{number molecules} = (\text{number of moles})(L)$$

$$N = nL = 0.1226 \text{ mol} (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$\boxed{N = 7.38 \times 10^{22}}$$

We can take the square root of Eq. 1.43 in order to find the root mean square speed of the molecules;

$$\overline{u^2} = \frac{3RT}{M} \quad (\text{Eq. 1.43})$$

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.028\,013\,4 \text{ kg mol}^{-1}}}$$

$$\boxed{\sqrt{\overline{u^2}} = 515.2 \text{ m s}^{-1}}$$

The average translational energy (for each molecule) is given by Eq. 1.44;

$$\bar{\epsilon}_k = \frac{1}{2} m \bar{u}^2 \rightarrow \frac{1}{2} \frac{(0.0280134 \text{ kg mol}^{-1})(515.2 \text{ m s}^{-1})^2}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\boxed{\bar{\epsilon}_k = 6.175 \times 10^{-21} \text{ J}}$$

It is possible to find the *total* translational kinetic energy in the system by using the equation;

$$E_{k_{\text{tot}}} = \frac{3}{2} nRT \quad (\text{Eq. 1.49})$$

$$E_{k_{\text{tot}}} = \frac{3}{2} (0.1226 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})$$

$$\boxed{E_{k_{\text{tot}}} = 456 \text{ J}}$$

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**1.31.** By what factor are the root-mean-square speeds changed if a gas is heated from 300 K to 400 K?

**Solution:**

Given:  $T_1 = 300$  K,  $T_2 = 400$  K

Required: change in root-mean-square speeds

Recall Eq. 1.43

$$\overline{u^2} = \frac{3RT}{M}$$

Remember that in problem 1.29 we outlined the relationship between  $\overline{u^2}$  and  $T$ . Using this information, it is possible to see that the following ratios are equivalent;

$$\frac{\sqrt{\overline{u_2^2}}}{\sqrt{\overline{u_1^2}}} = \frac{\sqrt{T_2}}{\sqrt{T_1}}$$

Now we can determine the magnitude of change in root-mean-square speed when moving from a lower to a higher temperature.

$$\frac{\sqrt{T_2}}{\sqrt{T_1}} = \frac{\sqrt{400}}{\sqrt{300}} = \sqrt{1.33}$$

$$\boxed{\frac{\sqrt{T_2}}{\sqrt{T_1}} = 1.15}$$

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**1.32.** The collision diameter of  $N_2$  is  $3.74 \times 10^{-10}$  m at 298.15 K and 101.325 kPa. Its average speed is  $474.6 \text{ m s}^{-1}$ . Calculate the mean free path, the average number of collisions  $Z_A$  experienced by one molecule in unit time, and the average number of collisions  $Z_{AA}$  per unit volume per unit time for  $N_2$ .

**Solution:**

Given:  $d_A = 3.74 \times 10^{-10}$  m,  $T = 298.15$  K,  $P = 101.325$  kPa,  $\bar{u}_A = 474.6 \text{ m s}^{-1}$

Required:  $\lambda, Z_A, Z_{AA}$

The mean free path is given by Eq. 1.68;

$$\lambda = \frac{V}{\sqrt{2}\pi d_A^2 N_A}$$

Using the ideal gas law,  $PV = nRT$ , and solving for  $V$ , a useful expression for the mean free path can be obtained;

$$V = \frac{nRT}{P}$$

Giving the mean free path as,

$$\lambda = \frac{\frac{nRT}{P}}{\sqrt{2}\pi d_A^2 N_A}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$\lambda = \frac{RT}{\sqrt{2}\pi d_A^2 LP}$$

$$\lambda = \frac{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1})(298.15 \cancel{\text{K}})}{\sqrt{2}\pi (3.74 \times 10^{-10} \text{ m})^2 (6.022 \times 10^{23} \cancel{\text{mol}^{-1}})(101325 \text{ Pa})}$$

$$\lambda = 6.537 \times 10^{-8} \text{ J m}^{-2} \text{ Pa}^{-1}$$

where  $1 \text{ J} = \text{kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ J}}{1 \text{ Pa}} = \frac{1 \cancel{\text{kg}} \text{ m}^2 \cancel{\text{s}^{-2}}}{1 \cancel{\text{kg}} \text{ m}^{-1} \cancel{\text{s}^{-2}}} = 1 \text{ m}^3$$

$$\lambda = 6.537 \times 10^{-8} \text{ m}^{-2} \text{ m}^3$$

$$\boxed{\lambda = 6.54 \times 10^{-8} \text{ m}}$$

The average number of collisions  $Z_A$  experienced by one molecule in unit time, also known as the collision frequency for one molecule is given by Eq. 1.66;

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A}{V} \quad (\text{SI unit : s}^{-1})$$

Using the ideal gas law  $PV = nRT$  and solving for  $V$ , a useful expression for  $Z_A$  can be obtained.

$$V = \frac{nRT}{P}$$

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A P}{nRT}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A L P}{RT}$$

$$Z_A = \frac{\sqrt{2}\pi (3.74 \times 10^{-10} \text{ m})^2 (474.6 \text{ m s}^{-1}) (6.022 \times 10^{23} \text{ mol}^{-1}) (101325 \text{ Pa}) \frac{1 \text{ Pa}}{1 \text{ J}}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})} = \frac{1 \text{ kg m}^{-1} \text{ s}^{-2}}{1 \text{ kg m}^2 \text{ s}^{-2}} = 1 \text{ m}^{-3}$$

$$Z_A = 7\,259\,759\,289 \text{ m}^3 \text{ s}^{-1} \text{ Pa J}^{-1}$$

$$\text{where } 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \text{ and } 1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$Z_A = 7.26 \times 10^9 \text{ m}^3 \text{ s}^{-1} \text{ m}^{-3}$$

$$\boxed{Z_A = 7.26 \times 10^9 \text{ s}^{-1}}$$

The average number of collisions  $Z_{AA}$  per unit volume per unit time for  $N_2$ , also known as the collision density is given by Eq. 1.65;

$$Z_{AA} = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A^2}{2V^2} \quad (\text{SI unit : m}^{-3} \text{ s}^{-1})$$

Using the ideal gas law  $PV = nRT$  and solving for  $V$ , a useful expression for  $Z_{AA}$  can be obtained;

$$V = \frac{nRT}{P}$$

$$Z_{AA} = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A^2 P^2}{2(nRT)^2}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$Z_{AA} = \frac{\pi d_A^2 \bar{u}_A L^2 P^2}{\sqrt{2}(RT)^2}$$

Solving for  $Z_{AA}$ ,

$$Z_{AA} = \frac{\pi (3.74 \times 10^{-10} \text{ m})^2 (474.6 \text{ m s}^{-1}) (6.022 \times 10^{23} \text{ mol}^{-1})^2 (101325 \text{ Pa})^2}{\sqrt{2} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})^2 (298.15 \text{ K})^2}$$

$$Z_{AA} = 8.93467 \times 10^{34} \text{ m}^3 \text{ s}^{-1} \text{ Pa}^2 \text{ J}^{-2}$$

where  $1 \text{ J} = \text{kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ Pa}^2}{1 \text{ J}^2} = \frac{1 \text{ kg}^2 \text{ m}^{-2} \text{ s}^{-4}}{1 \text{ kg}^2 \text{ m}^4 \text{ s}^{-4}} = 1 \text{ m}^{-6}$$

$$Z_{AA} = 8.93467 \times 10^{34} \text{ m}^3 \text{ s}^{-1} \text{ m}^{-6}$$

$$\boxed{Z_{AA} = 8.93 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}}$$

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**1.33.** Express the mean free path of a gas in terms of the variables pressure and temperature, which are more easily measured than the volume.

**Solution:**

$$\text{Given: } \lambda = \frac{V}{\sqrt{2}\pi d_A^2 N_A}$$

Required: mean free path in terms of  $P$  and  $T$

The mean free path is given by;

$$\lambda = \frac{V}{\sqrt{2}\pi d_A^2 N_A} \quad (\text{Eq. 1.68})$$

Using the ideal gas law  $PV = nRT$  and solving for  $V$ , a useful expression for the mean free path can be obtained;

$$V = \frac{nRT}{P}$$

$$\lambda = \frac{\frac{nRT}{P}}{\sqrt{2}\pi d_A^2 N_A}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$\boxed{\lambda = \frac{RT}{\sqrt{2}\pi d_A^2 LP}}$$

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**1.34.** Calculate  $Z_A$  and  $Z_{AA}$  for argon at 25 °C and a pressure of 1.00 bar using

$d = 3.84 \times 10^{-10}$  m obtained from X-ray crystallographic measurements.

**Solution:**

Given:  $d_A = 3.84 \times 10^{-10}$  m,  $T = 298.15$  K,  $P = 10^5$  Pa

Required:  $Z_A, Z_{AA}$

$Z_A$  is given by Eq. 1.66;

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A}{V} \quad (\text{SI unit : s}^{-1})$$

Using the ideal gas law  $PV = nRT$  and solving for  $V$ , a useful expression for  $Z_A$  can be obtained.

$$V = \frac{nRT}{P}$$

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A P}{nRT}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A L P}{RT}$$

To solve for  $Z_A$  the speed must first be found. The average speed is given in the *Key Equations* section of the chapter;

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

$$\bar{u} = \sqrt{\frac{8(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{\pi(39.948 \text{ g mol}^{-1} \times 10^{-3} \text{ kg g}^{-1})}}$$

$$\bar{u} = \sqrt{158\,021.4434 \text{ J kg}^{-1}}$$

$$\text{since } 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$\bar{u} = \sqrt{158\,021.4434 (\text{kg m}^2 \text{ s}^{-2}) \text{ kg}^{-1}}$$

$$\bar{u} = 397.519 \text{ m s}^{-1}$$

Solving for  $Z_A$  gives;

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A L P}{RT}$$

$$Z_A = \frac{\sqrt{2}\pi(3.84 \times 10^{-10} \text{ m})^2 (397.519 \text{ m s}^{-1})(6.022 \times 10^{23} \text{ mol}^{-1})(10\,000 \text{ Pa})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$Z_A = 6\,326\,376\,149 \text{ m}^3 \text{ s}^{-1} \text{ Pa J}^{-1}$$

$$\text{where } 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \text{ and } 1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$\frac{1 \text{ Pa}}{1 \text{ J}} = \frac{1 \text{ kg m}^{-1} \text{ s}^{-2}}{1 \text{ kg m}^2 \text{ s}^{-2}} = 1 \text{ m}^{-3}$$

$$Z_A = 6.33 \times 10^9 \text{ m}^3 \text{ s}^{-1} \text{ m}^{-3}$$

$$\boxed{Z_A = 6.33 \times 10^9 \text{ s}^{-1}}$$

$Z_{AA}$  is given by Eq. 1.65;



$$Z_{AA} = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A^2}{2V^2} \quad (\text{SI unit : m}^{-3} \text{ s}^{-1})$$

Using the ideal gas law  $PV = nRT$  and solving for  $V$ , an expression for  $Z_{AA}$  is as follows;

$$V = \frac{nRT}{P}$$

$$Z_{AA} = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A^2 P^2}{2(nRT)^2}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$Z_{AA} = \frac{\pi d_A^2 \bar{u}_A L^2 P^2}{\sqrt{2}(RT)^2}$$

Solving for  $Z_{AA}$  to get;

$$Z_{AA} = \frac{\pi (3.84 \times 10^{-10} \text{ m})^2 (397.519 \text{ m s}^{-1}) (6.022 \times 10^{23} \text{ mol}^{-1})^2 (10\,000 \text{ Pa})^2}{\sqrt{2} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})^2 (298.15 \text{ K})^2}$$

$$Z_{AA} = 7.68413 \times 10^{34} \text{ m}^3 \text{ s}^{-1} \text{ Pa}^2 \text{ J}^{-2}$$

since  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ Pa}^2}{1 \text{ J}^2} = \frac{1 \text{ kg}^2 \text{ m}^{-2} \text{ s}^{-4}}{1 \text{ kg}^2 \text{ m}^4 \text{ s}^{-4}} = 1 \text{ m}^{-6}$$

$$Z_{AA} = 7.68413 \times 10^{34} \text{ m}^3 \text{ s}^{-1} \text{ m}^{-6}$$

$$\boxed{Z_{AA} = 7.68 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}}$$

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**1.35.** Calculate the mean free path of Ar at 20 °C and 1.00 bar. The collision diameter

$$d = 3.84 \times 10^{-10} \text{ m.}$$

**Solution:**

Given:  $T = 20^\circ\text{C} = 293.15 \text{ K}$ ,  $P = 1.00 \text{ bar} = 10^5 \text{ Pa}$ ,  $d_A = 3.84 \times 10^{-10} \text{ m}$

Required:  $\lambda$

The mean free path is given by Eq. 1.68;

$$\lambda = \frac{V}{\sqrt{2}\pi d_A^2 N_A}$$

Using the ideal gas law  $PV = nRT$  and solving for  $V$ , a useful expression for the mean free path can be obtained.

$$V = \frac{nRT}{P}$$

$$\lambda = \frac{\frac{nRT}{P}}{\sqrt{2}\pi d_A^2 N_A}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$\lambda = \frac{RT}{\sqrt{2}\pi d_A^2 LP}$$

$$\lambda = \frac{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}})(293.15 \cancel{\text{K}})}{\sqrt{2}\pi (3.84 \times 10^{-10} \text{ m})^2 (6.022 \times 10^{23} \cancel{\text{mol}^{-1}})(10\,000 \text{ Pa})}$$

$$\lambda = 6.1781 \times 10^{-8} \text{ J m}^{-2} \text{ Pa}^{-1}$$

since  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ J}}{1 \text{ Pa}} = \frac{1 \cancel{\text{kg}} \cancel{\text{m}^2} \cancel{\text{s}^{-2}}}{1 \cancel{\text{kg}} \cancel{\text{m}^{-1}} \cancel{\text{s}^{-2}}} = 1 \text{ m}^3$$

$$\lambda = 6.1781 \times 10^{-8} \text{ m}^{-2} \text{ m}^3$$

$$\boxed{\lambda = 6.18 \times 10^{-8} \text{ m}}$$

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**1.36.** Hydrogen gas has a molecular collision diameter of 0.258 nm. Calculate the mean free path of hydrogen at 298.15 K and (a) 133.32 Pa, (b) 101.325 k Pa, and (c)  $1.0 \times 10^8$  Pa.

**Solution:**

Given:  $d_A = 0.258 \text{ nm} = 2.58 \times 10^{-10} \text{ m}$ ,  $T = 298.15 \text{ K}$

Required:  $\lambda$

The mean free path is given by Eq. 1.68;

$$\lambda = \frac{V}{\sqrt{2}\pi d_A^2 N_A}$$

Using the ideal gas law  $PV = nRT$  and solving for  $V$ , a useful expression for the mean free path can be obtained.

$$V = \frac{nRT}{P}$$

$$\lambda = \frac{\frac{nRT}{P}}{\sqrt{2}\pi d_A^2 N_A}$$

$$L = \frac{N_A}{n}, \text{ where } N_A \text{ is the number of particles}$$

$$\lambda = \frac{RT}{\sqrt{2}\pi d_A^2 LP}$$

Now using the fact that  $P = 133.32 \text{ Pa}$  we can make the appropriate substitutions to get;

$$\lambda = \frac{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}})(298.15 \cancel{\text{K}})}{\sqrt{2}\pi (2.58 \times 10^{-10} \text{ m})^2 (6.022 \times 10^{23} \cancel{\text{mol}^{-1}})(133.32 \text{ Pa})}$$

$$\lambda = 1.044 \times 10^{-4} \text{ J m}^{-2} \text{ Pa}^{-1}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ J}}{1 \text{ Pa}} = \frac{1 \cancel{\text{kg}} \cancel{\text{m}^2} \cancel{\text{s}^{-2}}}{1 \cancel{\text{kg}} \cancel{\text{m}^{-1}} \cancel{\text{s}^{-2}}} = 1 \text{ m}^3$$

$$\lambda = 1.044 \times 10^{-4} \text{ m}^{-2} \text{ m}^3$$

$$\boxed{\lambda = 1.044 \times 10^{-4} \text{ m}}$$

With the next pressure ( $P = 101.325 \text{ kPa}$ ) we can use the same method as outlined above;

$$\lambda = \frac{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}})(298.15 \cancel{\text{K}})}{\sqrt{2}\pi (2.58 \times 10^{-10} \text{ m})^2 (6.022 \times 10^{23} \cancel{\text{mol}^{-1}})(101\,325 \text{ Pa})}$$

$$\lambda = 1.37 \times 10^{-7} \text{ J m}^{-2} \text{ Pa}^{-1}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ J}}{1 \text{ Pa}} = \frac{1 \cancel{\text{kg}} \cancel{\text{m}^2} \cancel{\text{s}^{-2}}}{1 \cancel{\text{kg}} \cancel{\text{m}^{-1}} \cancel{\text{s}^{-2}}} = 1 \text{ m}^3$$

$$\lambda = 1.37 \times 10^{-7} \text{ m}^{-2} \text{ m}^3$$

$$\boxed{\lambda = 1.37 \times 10^{-7} \text{ m}}$$

For the final pressure  $P = 1.0 \times 10^8 \text{ Pa}$ ,

$$\lambda = \frac{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}})(298.15 \cancel{\text{K}})}{\sqrt{2}\pi (2.58 \times 10^{-10} \text{ m})^2 (6.022 \times 10^{23} \cancel{\text{mol}^{-1}})(1.0 \times 10^8 \text{ Pa})}$$

$$\lambda = 1.39 \times 10^{-10} \text{ J m}^{-2} \text{ Pa}^{-1}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ J}}{1 \text{ Pa}} = \frac{1 \cancel{\text{kg}} \cancel{\text{m}^2} \cancel{\text{s}^{-2}}}{1 \cancel{\text{kg}} \cancel{\text{m}^{-1}} \cancel{\text{s}^{-2}}} = 1 \text{ m}^3$$

$$\lambda = 1.39 \times 10^{-10} \text{ m}^{-2} \text{ m}^3$$

$$\boxed{\lambda = 1.39 \times 10^{-10} \text{ m}}$$

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**1.37.** In interstellar space it is estimated that atomic hydrogen exists at a concentration of one particle per cubic meter. If the collision diameter is  $2.5 \times 10^{-10}$  m, calculate the mean free path  $\lambda$ . The temperature of interstellar space is 2.7 K.

**Solution:**

Given:  $d_A = 2.50 \times 10^{-10}$  m,  $T = 2.7$  K,  $C = 1$  particle  $\text{m}^{-3}$

Required:  $\lambda$

The mean free path is given by Eq. 1.68;

$$\lambda = \frac{V}{\sqrt{2}\pi d_A^2 N_A}$$

Concentration is given by;

$$C = \frac{N_A}{V}, \text{ where } N_A \text{ is the number of particles}$$

Now it is possible to solve for  $\lambda$

$$\lambda = \frac{1}{\sqrt{2}\pi d_A^2 C}$$

$$\lambda = \frac{1}{\sqrt{2}\pi (2.50 \times 10^{-10} \text{ m})^2 (1 \text{ particle m}^{-3})}$$

$$\lambda = 3.60 \times 10^{18} \text{ m}$$

$$\boxed{\lambda = 3.60 \times 10^{18} \text{ m}}$$

*This is about a hundred times greater than the distance between the earth and the nearest star (Proxima Centauri)!*

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- 1.38.** Calculate the value of Avogadro's constant from a study made by Perrin [*Ann. Chem. Phys.*, 18, 1(1909)] in which he measured as a function of height the distribution of bright yellow colloidal gamboge (a gum resin) particles suspended in water. Some data at 15 °C are:

height, $z/10^{-6}$	5	35
---------------------	---	----

$N$ , relative number of gamboge particles at height $z$	100	47
--	-----	----

$$\rho_{\text{gamboge}} = 1.206 \text{ g cm}^{-3}$$

$$\rho_{\text{water}} = 0.999 \text{ g cm}^{-3} \text{ radius of gamboge particles, } r = 0.212 \times 10^{-6} \text{ m}$$

(Hint: Consider the particles to be gas molecules in a column of air and that the number of particles is proportional to the pressure.)

**Solution:**

Given: see above

Required: Avogadro's number,  $L$

Since we consider the gamboges particles to be proportional to the pressure, we can write;

$$\frac{dP}{P} = - \left( \frac{Mg}{RT} \right) dz \quad (\text{Eq. 1.74})$$

Here,  $g$  is the acceleration due to gravity. Taking the integral of both sides and simplifying gives;

$$\ln \frac{N}{N_0} = - \frac{Mg}{RT} \Delta z \text{ where } M = mL$$

This can then be substituted into the above equation to get;

$$\ln \frac{N}{N_0} = - \frac{mLg}{RT} \Delta z$$

Solving for  $L$ ;

$$L = - \frac{RT}{mg \Delta z} \ln \frac{N}{N_0}$$



Density is given by  $\rho = \frac{m}{V}$

Rearranging for the mass of the gamboges particle then gives;

$$m = \rho V$$

Where  $V$  is the volume of the gamboges particle. Since we know that volume is given by;  $V = \frac{4\pi r^3}{3}$

We can then define mass as follows;

$$m = \rho \frac{4\pi r^3}{3}$$

Now Avogadro's number can be expressed as;

$$L = - \frac{RT}{\left( \frac{4\pi}{3} \rho r^3 \right) g \Delta z} \ln \frac{N}{N_0}$$

Solving for Avogadro's number,

$$L = - \frac{(8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1})(288.15 \cancel{\text{K}})}{\left( \frac{4\pi}{3} (1.206 \cancel{\text{g cm}^{-3}} - 0.999 \cancel{\text{g cm}^{-3}}) \left( \times 10^3 \frac{\text{kg } \cancel{\text{m}^{-3}}}{\cancel{\text{g cm}^{-3}}} \right) (0.212 \times 10^{-6} \cancel{\text{m}})^3 \right) (9.81 \text{ m s}^{-2})} \times \frac{1}{(35 \times 10^{-6} \text{ m} - 5 \times 10^{-6} \text{ m})} \times \ln \frac{100}{47}$$

$$\boxed{L = 7.44 \times 10^{23} \text{ mol}^{-1}}$$

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**1.39.** Refer to Table 1.3 (p. 32) and write expressions and values for (a) the ratio  $\sqrt{u^2}/\bar{u}$ , and (b) the ratio  $\bar{u}/u_{mp}$ . Note that these ratios are independent of the mass and the temperature. How do the *differences* between them depend on these quantities?

**Solution:**

Given: Table 1.3

Required:  $\sqrt{u^2}/\bar{u}$  and  $\bar{u}/u_{mp}$

From Table 1.3 the root mean speed is  $\sqrt{u^2} = \sqrt{\frac{3k_B T}{m}}$ , and the average speed is  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$

$$\frac{\sqrt{u^2}}{\bar{u}} = \sqrt{\frac{3k_B T}{m}} \div \sqrt{\frac{8k_B T}{\pi m}}$$

$$\frac{\sqrt{u^2}}{\bar{u}} = \sqrt{\frac{3\cancel{k_B T}}{\cancel{m}}} \times \frac{\pi \cancel{m}}{8\cancel{k_B T}}$$

$$\frac{\sqrt{u^2}}{\bar{u}} = \sqrt{\frac{3\pi}{8}}$$

$$\boxed{\frac{\sqrt{u^2}}{\bar{u}} = 1.085}$$

From Table 1.3 the average speed is  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$  and the most probable speed is  $u_{mp} = \sqrt{\frac{2k_B T}{m}}$

$$\frac{\bar{u}}{u_{\text{mp}}} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}} \div \sqrt{\frac{2k_{\text{B}}T}{m}}$$

$$\frac{\bar{u}}{u_{\text{mp}}} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}} \times \frac{m}{2k_{\text{B}}T}$$

$$\frac{\bar{u}}{u_{\text{mp}}} = \sqrt{\frac{4}{\pi}}$$

$$\frac{\bar{u}}{u_{\text{mp}}} = \frac{2}{\sqrt{\pi}}$$

$$\boxed{\frac{\bar{u}}{u_{\text{mp}}} = 1.128}$$

The differences between  $\sqrt{u^2}$  and  $\bar{u}$  and between  $\bar{u}$  and  $u_{\text{mp}}$  increase with  $T$  and decrease with  $m$ .

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**1.40.** The speed that a body of any mass must have to escape from the earth is  $1.07 \times 10^4 \text{ m s}^{-1}$ . At what temperature would the average speed of (a) a  $\text{H}_2$  molecule, and (b) an  $\text{O}_2$  molecule be equal to this escape speed?

**Solution:**

Given:  $\bar{u} = 1.07 \times 10^4 \text{ m s}^{-1}$

Required:  $T_{\text{H}_2}$ ,  $T_{\text{O}_2}$

Average speed, as listed in Table 1.3, is given by  $\bar{u} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}$

By rearranging this equation, temperature can be described as;

$$T = \frac{\pi m \bar{u}^2}{8k_{\text{B}}}$$

The mass is given by  $m = \frac{M}{L}$  and by using this expression, the temperature can be simplified to;

$$T = \frac{\pi \bar{u}^2 M}{8k_{\text{B}} L} \text{ where, } k_{\text{B}} = \frac{R}{L}$$

$$T = \frac{\pi \bar{u}^2 M}{8R}$$

a. Solving for  $T_{\text{H}_2}$ ;

$$T_{\text{H}_2} = \frac{\pi (1.07 \times 10^4 \text{ m s}^{-1})^2 (2 \times 1.00794 \cancel{\text{ g mol}^{-1}}) \times 10^{-3} \text{ kg } \cancel{\text{ g}^{-1}}}{8 (8.3145 \text{ J K}^{-1} \cancel{\text{ mol}^{-1}})}$$

$$T_{\text{H}_2} = 10\,898 \text{ m}^2 \text{ s}^{-2} \text{ kg J}^{-1} \text{ K}$$

$$\text{where } 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$T_{\text{H}_2} = 10\,898 \cancel{\text{ m}^2 \text{ s}^{-2} \text{ kg}} (\cancel{\text{ kg}^{-1} \text{ m}^{-2} \text{ s}^2}) \text{ K}$$

$$T_{\text{H}_2} = 10\,898 \text{ K}$$

$$\boxed{T_{\text{H}_2} = 1.09 \times 10^4 \text{ K}}$$

b. Solving for  $T_{\text{O}_2}$ ;

$$T_{\text{O}_2} = \frac{\pi (1.07 \times 10^4 \text{ m s}^{-1})^2 (2 \times 15.9994 \cancel{\text{ g mol}^{-1}}) \times 10^{-3} \text{ kg } \cancel{\text{ g}^{-1}}}{8 (8.3145 \text{ J K}^{-1} \cancel{\text{ mol}^{-1}})}$$

$$T_{\text{O}_2} = 172\,992 \text{ m}^2 \text{ s}^{-2} \text{ kg J}^{-1} \text{ K}$$

$$\text{where } 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$T_{\text{O}_2} = 172\,992 \cancel{\text{ m}^2 \text{ s}^{-2} \text{ kg}} (\cancel{\text{ kg}^{-1} \text{ m}^{-2} \text{ s}^2}) \text{ K}$$

$$T_{\text{O}_2} = 172\,992 \text{ K}$$

$$\boxed{T_{\text{O}_2} = 1.73 \times 10^5 \text{ K}}$$

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- 1.41.** a. For  $\text{H}_2$  gas at  $25^\circ\text{C}$ , calculate the ratio of the fraction of molecules that have a speed  $2\bar{u}$  to the fraction that have the average speed  $\bar{u}$ . How does this ratio depend on the mass of the molecules and the temperature?
- b. Calculate the ratio of the fraction of the molecules that have the average speed  $\bar{u}_{100^\circ\text{C}}$  at  $100^\circ\text{C}$  to the fraction that have the average speed  $\bar{u}_{25^\circ\text{C}}$  at  $25^\circ\text{C}$ . How does this ratio depend on the mass?

**Solution:**

Given:  $T = 25^\circ\text{C} = 298.15\text{K}$

Required: a.  $\frac{dN_{\bar{u}_1}}{N_{\bar{u}_1}} / \frac{dN_{\bar{u}_2}}{N_{\bar{u}_2}}$ , where  $\bar{u}_1 = 2\bar{u}$ ,  $\bar{u}_2 = \bar{u}$ ,  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$

b.  $\frac{dN_{\bar{u}_1}}{N_{\bar{u}_1}} / \frac{dN_{\bar{u}_2}}{N_{\bar{u}_2}}$  where  $\bar{u}_1 = \bar{u}_{100^\circ\text{C}}$ ,  $\bar{u}_2 = \bar{u}_{25^\circ\text{C}}$ ,  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$

a) The key words in this problem are *ratio of the fractions*, therefore we use the Boltzmann distribution. The Boltzmann distribution is

given by Eq. 1.91;  $\frac{dN}{N} = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mu^2/2k_B T} u^2 du$

Solving for the ratio;

$$\frac{\frac{dN_{\bar{u}_1}}{N_{\bar{u}_1}}}{\frac{dN_{\bar{u}_2}}{N_{\bar{u}_2}}} = \frac{4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-m\bar{u}_1^2/2k_B T} \bar{u}_1^2 d\bar{u}}{4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-m\bar{u}_2^2/2k_B T} \bar{u}_2^2 d\bar{u}}$$

$$\frac{dN_{\bar{u}_1}}{N_{\bar{u}_1}} / \frac{dN_{\bar{u}_2}}{N_{\bar{u}_2}} = e^{-m(\bar{u}_1^2 - \bar{u}_2^2)/2k_B T} \left( \frac{\bar{u}_1^2}{\bar{u}_2^2} \right)$$

where  $\bar{u}_1 = 2\bar{u}$ ,  $\bar{u}_2 = \bar{u}$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = e^{-m((2\bar{u})^2 - \bar{u}^2)/2k_B T} \left( \frac{(2\bar{u})^2}{\bar{u}^2} \right)$$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = e^{-m(4\bar{u}^2 - \bar{u}^2)/2k_B T} \left( \frac{4\cancel{\bar{u}^2}}{\cancel{\bar{u}^2}} \right)$$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = 4e^{-m(3\bar{u}^2)/2k_B T}$$

since  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$ , we can substitute for the average speed;

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = 4e^{-m\left(3\left(\sqrt{\frac{8k_B T}{\pi m}}\right)^2\right)/2k_B T}$$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = 4e^{-m\left(\left(\frac{24k_B T}{\pi m}\right)\right)\left(\frac{1}{2k_B T}\right)}$$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = 4e^{-\frac{12}{\pi}}$$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = 0.087\,735\,885$$

$$\boxed{\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = 8.77 \times 10^{-2}}$$

It is now possible to see that the ratio is independent of mass and temperature of the molecules.

b)

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = \frac{4\pi \left( \frac{m}{2\pi k_B} \right)^{3/2} \left( \frac{1}{T_{100^\circ\text{C}}} \right)^{3/2} e^{-mu_1^2/2k_B T_{100^\circ\text{C}}} \cancel{u_1^2 du_1}}{4\pi \left( \frac{m}{2\pi k_B} \right)^{3/2} \left( \frac{1}{T_{25^\circ\text{C}}} \right)^{3/2} e^{-mu_2^2/2k_B T_{25^\circ\text{C}}} \cancel{u_2^2 du_2}}$$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = \frac{\left( \frac{1}{T_{100^\circ\text{C}}} \right)^{3/2}}{\left( \frac{1}{T_{25^\circ\text{C}}} \right)^{3/2}} e^{\frac{-m}{2k_B} \left( \frac{u_1^2}{T_{100^\circ\text{C}}} - \frac{u_2^2}{T_{25^\circ\text{C}}} \right)} \left( \frac{u_1^2}{u_2^2} \right)$$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = \left( \frac{T_{100^\circ\text{C}}}{T_{25^\circ\text{C}}} \right)^{-3/2} e^{\frac{-m}{2k_B} \left( \frac{u_1^2}{T_{100^\circ\text{C}}} - \frac{u_2^2}{T_{25^\circ\text{C}}} \right)} \left( \frac{u_1^2}{u_2^2} \right)$$

where  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$

$$\frac{dN_{u_1}^-}{N_{u_1}^-} \bigg/ \frac{dN_{u_2}^-}{N_{u_2}^-} = \left( \frac{T_{100^\circ\text{C}}}{T_{25^\circ\text{C}}} \right)^{-3/2} e^{\frac{-m}{2k_B} \left( \frac{\left( \sqrt{\frac{8k_B T_{100^\circ\text{C}}}{\pi m}} \right)^2}{T_{100^\circ\text{C}}} - \frac{\left( \sqrt{\frac{8k_B T_{25^\circ\text{C}}}{\pi m}} \right)^2}{T_{25^\circ\text{C}}} \right)} \left( \frac{\left( \sqrt{\frac{8k_B T_{100^\circ\text{C}}}{\pi m}} \right)^2}{\left( \sqrt{\frac{8k_B T_{25^\circ\text{C}}}{\pi m}} \right)^2} \right)$$



$$\frac{dN_{u1}^-}{N_{u1}^-} / \frac{dN_{u2}^-}{N_{u2}^-} = \left( \frac{T_{100^\circ\text{C}}}{T_{25^\circ\text{C}}} \right)^{-3/2} e^{\frac{-m}{2k_B} \left( \frac{8k_B T_{100^\circ\text{C}}}{\pi m} - \frac{8k_B T_{25^\circ\text{C}}}{\pi m} \right)} \left( \frac{T_{100^\circ\text{C}}}{T_{25^\circ\text{C}}} \right)$$

$$\frac{dN_{u1}^-}{N_{u1}^-} / \frac{dN_{u2}^-}{N_{u2}^-} = \left( \frac{T_{100^\circ\text{C}}}{T_{25^\circ\text{C}}} \right)^{-1/2} e^{\left( \frac{-1}{2} \times \frac{m}{k_B} \right) \left( \frac{8}{\pi} \times \frac{k_B}{m} \right) \left( \left( \frac{T_{100^\circ\text{C}}}{T_{100^\circ\text{C}}} \right) - \left( \frac{T_{25^\circ\text{C}}}{T_{25^\circ\text{C}}} \right) \right)}$$

$$\frac{dN_{u1}^-}{N_{u1}^-} / \frac{dN_{u2}^-}{N_{u2}^-} = \left( \frac{T_{100^\circ\text{C}}}{T_{25^\circ\text{C}}} \right)^{-1/2} e^{\left( \frac{-4}{\pi} \right) (0)}$$

$$\frac{dN_{u1}^-}{N_{u1}^-} / \frac{dN_{u2}^-}{N_{u2}^-} = \left( \frac{T_{100^\circ\text{C}}}{T_{25^\circ\text{C}}} \right)^{-1/2}$$

$$\frac{dN_{u1}^-}{N_{u1}^-} / \frac{dN_{u2}^-}{N_{u2}^-} = \left( \frac{373.15 \text{ K}}{298.15 \text{ K}} \right)^{-1/2}$$

$$\frac{dN_{u1}^-}{N_{u1}^-} / \frac{dN_{u2}^-}{N_{u2}^-} = 0.8938727$$

$$\boxed{\frac{dN_{u1}^-}{N_{u1}^-} / \frac{dN_{u2}^-}{N_{u2}^-} = 0.894}$$

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**1.42.** Suppose that two ideal gases are heated to different temperatures such that their pressures and vapor densities are the same. What is the relationship between their average molecular speeds?

**Solution:**

Given: Two Ideal Gases,  $\rho$ ,  $P$  and  $T$

Required: the relationship between the average speeds of two ideal gases

To solve this problem, we use the Ideal Gas Law to eliminate the temperature dependence from the equation for average speed. This is true because for  $T_1$  and  $T_2$ ,  $P_1 = P_2 \equiv P$  and  $\rho_1 = \rho_2 \equiv \rho$ ;

$$PV = nRT$$

$$T = \frac{PV}{nR}$$

$$\text{where } R = k_B L$$

$$T = \frac{PV}{nk_B L}$$

Substituting the above expression into the equation for average speed, as given in Table 1.3, and simplifying, gives the relationship between the average speed of two ideal gases that are heated to different temperatures such that their pressures and vapor densities are the same.

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\bar{u} = \sqrt{\frac{8 \cancel{k_B} PV}{\pi m n \cancel{k_B} L}}$$

$$\bar{u} = \sqrt{\frac{8PV}{\pi mnL}}$$

$$\text{where } \rho = \frac{N}{V} = \frac{nmL}{V}$$

$$\bar{u} = \sqrt{\frac{8P}{\pi \rho}}$$

Since  $P$  and  $\rho$  are the same, the average speed is the same for both gases.

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**1.43. a.** If  $\bar{u}_{25^\circ\text{C}}$  is the average speed of the molecules in a gas at  $25^\circ\text{C}$ , calculate the ratio of the fraction that will have the speed  $\bar{u}_{25^\circ\text{C}}$  at  $100^\circ\text{C}$  to the fraction that will have the same speed at  $25^\circ\text{C}$ .

**b.** Repeat this calculation for a speed of  $10 \bar{u}_{25^\circ\text{C}}$ .

**Solution:**

Given:  $T_{100^\circ\text{C}} = 373.15 \text{ K}$ ,  $T_{25^\circ\text{C}} = 298.15 \text{ K}$

Required: a)  $\frac{dN_{T_{100^\circ\text{C}}}}{N_{T_{100^\circ\text{C}}}} \bigg/ \frac{dN_{T_{25^\circ\text{C}}}}{N_{T_{25^\circ\text{C}}}}$

b)  $\frac{dN_{T_{100^\circ\text{C}}}}{N_{T_{100^\circ\text{C}}}} \bigg/ \frac{dN_{T_{25^\circ\text{C}}}}{N_{T_{25^\circ\text{C}}}}$

The key words in this problem are *ratio of the fractions*, therefore we use the Boltzmann distribution. The Boltzmann distribution is given

by Eq. 1.91;  $\frac{dN}{N} = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mu^2/2k_B T} u^2 du$ , where the average speed of molecules is given in Table 1.3 as  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$

Solving for the ratio we get;

$$\frac{\frac{dN_{T_{100^\circ\text{C}}}}{N_{T_{100^\circ\text{C}}}}}{\frac{dN_{T_{25^\circ\text{C}}}}{N_{T_{25^\circ\text{C}}}}} = \frac{4\pi \left( \frac{m}{2\pi k_B} \right)^{3/2} \left( \frac{1}{T_{100^\circ\text{C}}} \right)^{3/2} e^{-m(\bar{u}_{25^\circ\text{C}})^2/2k_B T_{100^\circ\text{C}}} (\bar{u}_{100^\circ\text{C}})^2 d\bar{u}}{4\pi \left( \frac{m}{2\pi k_B} \right)^{3/2} \left( \frac{1}{T_{25^\circ\text{C}}} \right)^{3/2} e^{-m(\bar{u}_{25^\circ\text{C}})^2/2k_B T_{25^\circ\text{C}}} (\bar{u}_{25^\circ\text{C}})^2 d\bar{u}}$$

$$\frac{\frac{dN_{T_{100^\circ\text{C}}}}{N_{T_{100^\circ\text{C}}}}}{\frac{dN_{T_{25^\circ\text{C}}}}{N_{T_{25^\circ\text{C}}}}} = \frac{\left( \frac{1}{T_{100^\circ\text{C}}} \right)^{3/2} e^{-\frac{m}{2k_B} \left( \frac{(\bar{u}_{25^\circ\text{C}})^2}{T_{100^\circ\text{C}}} - \frac{(\bar{u}_{25^\circ\text{C}})^2}{T_{25^\circ\text{C}}} \right)} (\bar{u}_{100^\circ\text{C}})^2}{\left( \frac{1}{T_{25^\circ\text{C}}} \right)^{3/2} (\bar{u}_{25^\circ\text{C}})^2}$$

where  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-3/2} e^{\frac{-m}{2k_B} \left( \frac{\left( \sqrt{\frac{8k_B T_{25}^{\circ}\text{C}}{\pi m}} \right)^2}{T_{100}^{\circ}\text{C}} - \frac{\left( \sqrt{\frac{8k_B T_{25}^{\circ}\text{C}}{\pi m}} \right)^2}{T_{25}^{\circ}\text{C}} \right)} \frac{\left( \sqrt{\frac{8k_B T_{100}^{\circ}\text{C}}{\pi m}} \right)^2}{\left( \sqrt{\frac{8k_B T_{25}^{\circ}\text{C}}{\pi m}} \right)^2}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-3/2} e^{\frac{-m}{2k_B} \left( \frac{\left( \frac{8k_B T_{25}^{\circ}\text{C}}{\pi m} \right)}{T_{100}^{\circ}\text{C}} - \frac{\left( \frac{8k_B T_{25}^{\circ}\text{C}}{\pi m} \right)}{T_{25}^{\circ}\text{C}} \right)} \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-1/2} e^{\left( \frac{-1}{2} \times \frac{m}{k_B} \right) \left( \frac{8}{\pi} \times \frac{k_B}{m} \right) \left( \frac{T_{25}^{\circ}\text{C}}{T_{100}^{\circ}\text{C}} - \frac{T_{25}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-1/2} e^{\left( \frac{-4}{\pi} \right) \left( \frac{T_{25}^{\circ}\text{C}}{T_{100}^{\circ}\text{C}} - 1 \right)}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{373.15 \text{ K}}{298.15 \text{ K}} \right)^{-1/2} e^{\left( \frac{-4}{\pi} \right) \left( \frac{298.15 \text{ K}}{373.15 \text{ K}} - 1 \right)}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = 1.154\,559$$

$$\boxed{\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = 1.155}$$

At a speed of  $10 \bar{u}_{25}^{\circ}\text{C}$ ;

$$\frac{\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}}}{\frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}}} = \frac{\cancel{4\pi\left(\frac{m}{2\pi k_B}\right)^{3/2}} \left(\frac{1}{T_{100}^{\circ}\text{C}}\right)^{3/2} e^{-m(\bar{u}_{25}^{\circ}\text{C})^2/2k_B T_{100}^{\circ}\text{C}} (\bar{u}_{100}^{\circ}\text{C})^2 du}{\cancel{4\pi\left(\frac{m}{2\pi k_B}\right)^{3/2}} \left(\frac{1}{T_{25}^{\circ}\text{C}}\right)^{3/2} e^{-m(\bar{u}_{25}^{\circ}\text{C})^2/2k_B T_{25}^{\circ}\text{C}} (\bar{u}_{25}^{\circ}\text{C})^2 du}$$

$$\frac{\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}}}{\frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}}} = \frac{\left(\frac{1}{T_{100}^{\circ}\text{C}}\right)^{3/2} e^{\frac{-m}{2k_B}\left(\frac{(10\bar{u}_{25}^{\circ}\text{C})^2}{T_{100}^{\circ}\text{C}} - \frac{(\bar{u}_{25}^{\circ}\text{C})^2}{T_{25}^{\circ}\text{C}}\right)} (\bar{u}_{100}^{\circ}\text{C})^2}{\left(\frac{1}{T_{25}^{\circ}\text{C}}\right)^{3/2} (\bar{u}_{25}^{\circ}\text{C})^2}$$

where  $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-3/2} e^{\left( \frac{-m}{2k_B} \left( \frac{10 \sqrt{\frac{8k_B T_{25}^{\circ}\text{C}}{\pi m}}}{T_{100}^{\circ}\text{C}} - \frac{\sqrt{\frac{8k_B T_{25}^{\circ}\text{C}}{\pi m}}}{T_{25}^{\circ}\text{C}} \right)^2 \right)} \frac{\left( \sqrt{\frac{8k_B T_{100}^{\circ}\text{C}}{\pi m}} \right)^2}{\left( \sqrt{\frac{8k_B T_{25}^{\circ}\text{C}}{\pi m}} \right)^2}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-3/2} e^{\left( \frac{-m}{2k_B} \left( \frac{100 \left( \frac{8k_B T_{25}^{\circ}\text{C}}{\pi m} \right)}{T_{100}^{\circ}\text{C}} - \frac{\left( \frac{8k_B T_{25}^{\circ}\text{C}}{\pi m} \right)}{T_{25}^{\circ}\text{C}} \right) \right)} \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-1/2} e^{\left( \frac{-1}{2} \times \frac{m}{k_B} \left( \frac{8}{\pi} \times \frac{k_B}{m} \right) \left( \frac{100 T_{25}^{\circ}\text{C}}{T_{100}^{\circ}\text{C}} - \frac{T_{25}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right) \right)}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{T_{100}^{\circ}\text{C}}{T_{25}^{\circ}\text{C}} \right)^{-1/2} e^{\left( \frac{-4}{\pi} \left( \frac{100 T_{25}^{\circ}\text{C}}{T_{100}^{\circ}\text{C}} - 1 \right) \right)}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = \left( \frac{373.15 \text{ K}}{298.15 \text{ K}} \right)^{-1/2} e^{\left( \frac{-4}{\pi} \left( \frac{100 \times 298.15 \text{ K}}{373.15 \text{ K}} - 1 \right) \right)}$$

$$\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = 2.09987 \times 10^{-44}$$

$$\boxed{\frac{dN_{T_{100}^{\circ}\text{C}}}{N_{T_{100}^{\circ}\text{C}}} \bigg/ \frac{dN_{T_{25}^{\circ}\text{C}}}{N_{T_{25}^{\circ}\text{C}}} = 2.10 \times 10^{-44}}$$

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**1.44.** On the basis of Eq. 1.80 with  $\beta = 1/k_B T$ , derive an expression for the fraction of molecules in a one-dimensional gas having speeds between  $u_x$  and  $u_x + du_x$ . What is the most probable speed?

**Solution:**

Given:  $\beta = 1/k_B T$ ,  $dP_x = B e^{-mu_x^2 \beta / 2} du_x$

Required:  $\frac{dN}{N}$ , the fraction of molecules in a one-dimensional gas

Using Eq. 1.80, the fraction of molecules in a one-dimensional gas having speeds between  $u_x$  and  $u_x + du_x$  can be written as;

$$\frac{dN}{N} = \frac{dP_x}{P} = \frac{B e^{-mu_x^2 \beta / 2} du_x}{\int_0^{\infty} B e^{-mu_x^2 \beta / 2} du_x}$$

Using  $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left( \frac{\pi}{a} \right)^{1/2}$  from the appendix in Chapter 1, the denominator can be simplified.

$$\int_0^{\infty} B e^{-mu_x^2 \beta / 2} du_x = \frac{B}{2} \left( \frac{2\pi}{m\beta} \right)^{1/2}$$



$$\frac{dN}{N} = \frac{B e^{-mu_x^2 \beta / 2} du_x}{\frac{B}{2} \left( \frac{2\pi}{m\beta} \right)^{1/2}}$$

$$\frac{dN}{N} = \frac{2B e^{-mu_x^2 \beta / 2}}{B} \left( \frac{2\pi}{m\beta} \right)^{-1/2} du_x$$

$$\frac{dN}{N} = 2e^{-mu_x^2 \beta / 2} \left( \frac{m\beta}{2\pi} \right)^{1/2} du_x$$

$$\text{where } \beta = \frac{1}{k_B T}$$

$$\frac{dN}{N} = 2e^{-mu_x^2 \frac{1}{2k_B T}} \left( \frac{m}{2\pi k_B T} \right)^{1/2} du_x$$

$$\boxed{\frac{dN}{N} = e^{-mu_x^2 \frac{1}{2k_B T}} \left( \frac{2m}{\pi k_B T} \right)^{1/2} du_x}$$

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**1.45.** Derive an expression for the fraction of molecules in a one-dimensional gas having energies between  $\varepsilon_x$  and  $\varepsilon_x + d\varepsilon_x$ . Also, obtain an expression for the average energy  $\bar{\varepsilon}_x$ .

**Solution:**

Given:  $\frac{dN}{N} = e^{-mu_x^2 \frac{1}{2k_B T}} \left( \frac{2m}{\pi k_B T} \right)^{1/2} du_x$  (from problem 1.44)

Required:  $\frac{dN}{N}$ , the fraction of molecules in a one-dimensional gas

Using Eq. 1.93,  $\varepsilon_x = \frac{1}{2} mu^2$ , the fraction of molecules in a one-dimensional gas having speeds between  $u_x$  and  $u_x + du_x$

,  $\frac{dN}{N} = e^{-mu_x^2 \frac{1}{2k_B T}} \left( \frac{2m}{\pi k_B T} \right)^{1/2} du_x$  (from problem 1.44), can be converted into the fraction molecules having energies between  $\varepsilon_x$  and  $\varepsilon_x + d\varepsilon_x$ ;

$$\varepsilon_x = \frac{1}{2} m u_x^2$$

$$u_x = \sqrt{\frac{2\varepsilon_x}{m}}$$

$$\frac{du_x}{d\varepsilon_x} = \frac{1}{2} \left( \frac{2\varepsilon_x}{m} \right)^{-\frac{1}{2}} \left( \frac{2}{m} \right)$$

$$\frac{du_x}{d\varepsilon_x} = \frac{1}{m} \left( \frac{2\varepsilon_x}{m} \right)^{-\frac{1}{2}}$$

$$\frac{du_x}{d\varepsilon_x} = \frac{1}{m} \left( \frac{1}{m} \right)^{-\frac{1}{2}} (2\varepsilon_x)^{-\frac{1}{2}}$$

$$\frac{du_x}{d\varepsilon_x} = \left( \frac{1}{m} \right)^{\frac{1}{2}} (2\varepsilon_x)^{-\frac{1}{2}}$$

$$\frac{du_x}{d\varepsilon_x} = (2m\varepsilon_x)^{-\frac{1}{2}}$$

$$du_x = (2m\varepsilon_x)^{-\frac{1}{2}} d\varepsilon_x$$

$$\boxed{\frac{dN}{N} = e^{-\frac{\varepsilon_x}{k_B T}} \left( \frac{1}{\pi k_B T \varepsilon_x} \right)^{1/2} d\varepsilon_x}$$

The average energy is given by;

$$\bar{\varepsilon} = \int_0^{\infty} \varepsilon \frac{dN}{N} \quad (\text{Eq. 1.97})$$

Tailoring the above equation to this particular situation, we get;

$$\overline{\varepsilon_x} = \int_0^\infty \varepsilon_x \frac{dN_x}{N}$$

$$\overline{\varepsilon_x} = \int_0^\infty \varepsilon_x \left( e^{-\frac{\varepsilon_x}{k_B T}} \left( \frac{1}{\pi k_B T \varepsilon_x} \right)^{1/2} d\varepsilon_x \right)$$

$$\overline{\varepsilon_x} = \int_0^\infty \left( \frac{1}{\pi k_B T} \right)^{1/2} e^{-\frac{\varepsilon_x}{k_B T}} \varepsilon_x^{1/2} d\varepsilon_x$$

Using  $\int_0^\infty e^{-ax} x^{1/2} dx = \frac{1}{2a} \left( \frac{\pi}{a} \right)^{1/2}$  from the appendix in Chapter 1, the expression can be simplified.

$$\int_0^\infty e^{-\frac{\varepsilon_x}{k_B T}} \varepsilon_x^{1/2} d\varepsilon_x = \frac{1}{2} k_B T (\pi k_B T)^{1/2}$$

$$\overline{\varepsilon_x} = \left( \frac{1}{\pi k_B T} \right)^{1/2} \frac{1}{2} k_B T (\pi k_B T)^{1/2}$$

$$\overline{\varepsilon_x} = \frac{1}{2} k_B T$$

Solving for the fraction of energies we get;

$$\frac{dN}{N} = e^{-m \left( \frac{2\varepsilon_x}{m} \right) \frac{1}{2k_B T}} \left( \frac{2m}{\pi k_B T} \right)^{1/2} (2m\varepsilon_x)^{-\frac{1}{2}} d\varepsilon_x$$

$$\frac{dN}{N} = e^{-\frac{\varepsilon_x}{k_B T}} \left( \frac{2m}{\pi k_B T} \times \frac{1}{2m\varepsilon_x} \right)^{1/2} d\varepsilon_x$$

$$\frac{dN}{N} = e^{-\frac{\varepsilon_x}{k_B T}} \left( \frac{1}{\pi k_B T \varepsilon_x} \right)^{1/2} d\varepsilon_x$$

$$\boxed{\overline{\varepsilon_x} = \frac{1}{2} k_B T}$$

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**1.46.** Derive an expression for the fraction of molecules in a two-dimensional gas having speeds between  $u$  and  $u + du$ . (*Hint:* Proceed by analogy with the derivation of Eq. 1.91.) Then obtain the expression for the fraction having energies between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ . What fraction will have energies in excess of  $\varepsilon^*$ ?

**Solution:**

Given: Two dimensional gas:  $\frac{dN}{N} = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mu^2/2k_B T} u^2 du$

Required:  $\frac{dN}{N}$ , the fraction of molecules in a two-dimensional gas

The following equations:

$$dP_x = B e^{-mu_x^2 \beta / 2} du_x \quad (\text{Eq. 1.80})$$

$$dP_y = B e^{-mu_y^2 \beta / 2} du_y \quad (\text{Eq. 1.81})$$

can be combined to give an expression reflecting the probability that the two components of speed have values between  $u_x$  and  $u_x + du_x$ ,  $u_y$  and  $u_y + du_y$ .

$$dP_x dP_y = \left( B e^{-mu_x^2 \beta / 2} du_x \right) \left( B e^{-mu_y^2 \beta / 2} du_y \right)$$

$$dP_x dP_y = B^2 e^{-m(u_x^2 + u_y^2) \beta / 2} du_x du_y$$

Using polar coordinates, we consider a circular shell of radius  $u$  and replace  $du_x du_y$  by  $2\pi u du$ , and take  $u^2 = u_x^2 + u_y^2$

We can then rewrite  $dP_x dP_y = B^2 e^{-m(u_x^2 + u_y^2) \beta / 2} du_x du_y$  as  $dP = 2\pi B^2 e^{-mu^2 \beta / 2} u du$

Using Eq. 1.91, an expression for the speed can be obtained;

$$\frac{dN}{N} = \frac{dP}{P} = \frac{2\pi B^2 e^{-mu^2 \beta/2} u du}{\int_0^\infty 2\pi B^2 e^{-mu^2 \beta/2} u du}$$

$$\frac{dN}{N} = \frac{2\pi B^2 e^{-mu^2 \beta/2} u du}{2\pi B^2 \int_0^\infty e^{-mu^2 \beta/2} u du}$$

$$\frac{dN}{N} = \frac{e^{-mu^2 \beta/2} u du}{\int_0^\infty e^{-mu^2 \beta/2} u du}$$

Using  $\int_0^\infty e^{-ax^2} x dx = \frac{1}{2a}$  from the appendix to Chapter 1, the denominator can be simplified.

$$\int_0^\infty e^{-mu^2 \beta/2} u du = \frac{1}{2} \left( \frac{2}{m\beta} \right)$$

$$\int_0^\infty e^{-mu^2 \beta/2} u du = \frac{1}{m\beta}$$

$$\frac{dN}{N} = \frac{e^{-mu^2 \beta/2} u du}{\frac{1}{m\beta}}$$

$$\frac{dN}{N} = m\beta e^{-mu^2 \beta/2} u du$$

$$\text{where } \beta = \frac{1}{k_B T}$$

$$\frac{dN}{N} = \frac{m}{k_B T} e^{-\frac{mu^2}{2k_B T}} u du$$

$$\frac{dN}{N} = \frac{m}{k_B T} e^{-\frac{mu^2}{2k_B T}} u du$$

Using Eq. 1.93,  $\varepsilon = \frac{1}{2}mu^2$ , the fraction of molecules in two dimensional gas having speeds between  $u$  and  $u + du$ , can be converted into the fraction molecules having energies between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ ,

$$\varepsilon = \frac{1}{2}mu^2$$

$$u = \left( \frac{2\varepsilon}{m} \right)^{\frac{1}{2}}$$

$$\frac{du}{d\varepsilon} = \frac{1}{2} \left( \frac{2\varepsilon}{m} \right)^{-\frac{1}{2}} \left( \frac{2}{m} \right)$$

$$\frac{du}{d\varepsilon} = \frac{1}{m} \left( \frac{2\varepsilon}{m} \right)^{-\frac{1}{2}}$$

$$\frac{du}{d\varepsilon} = \frac{1}{m} \left( \frac{1}{m} \right)^{-\frac{1}{2}} (2\varepsilon)^{-\frac{1}{2}}$$

$$\frac{du}{d\varepsilon} = \left( \frac{1}{m} \right)^{\frac{1}{2}} (2\varepsilon)^{-\frac{1}{2}}$$

$$\frac{du}{d\varepsilon} = (2m\varepsilon)^{-\frac{1}{2}}$$

$$du = (2m\varepsilon)^{-\frac{1}{2}} d\varepsilon$$

We can now solve for the fraction of energies;

$$\frac{dN}{N} = \frac{m}{k_B T} e^{-\frac{mu^2}{2k_B T}} u du$$

$$\frac{dN}{N} = \frac{m}{k_B T} e^{-m \left( \frac{2\varepsilon}{m} \right) \frac{1}{2k_B T}} \left( \frac{2\varepsilon}{m} \right)^{\frac{1}{2}} (2m\varepsilon)^{-\frac{1}{2}} d\varepsilon$$

$$\frac{dN}{N} = \frac{m}{k_B T} e^{-\frac{\varepsilon}{k_B T}} \left( \frac{2\varepsilon}{m} \right)^{\frac{1}{2}} (2m\varepsilon)^{-\frac{1}{2}} d\varepsilon$$

$$\frac{dN}{N} = \frac{m}{k_B T} e^{-\frac{\varepsilon}{k_B T}} \left( \cancel{m^{\frac{1}{2}}} \right) \left( \cancel{m^{\frac{1}{2}}} \right) d\varepsilon$$

$$\frac{dN}{N} = \frac{1}{k_B T} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$\boxed{\frac{dN}{N} = \frac{1}{k_B T} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon}$$

The fraction of molecules with energy greater than  $\varepsilon^*$  can be obtained from the expression

$$\frac{N^*}{N} = \int_{\varepsilon^*}^{\infty} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$\frac{N^*}{N} = e^{-\frac{\varepsilon}{k_B T}} \bigg|_{\varepsilon^*}^{\infty}$$

$$\boxed{\frac{N^*}{N} = e^{-\frac{\varepsilon^*}{k_B T}}}$$

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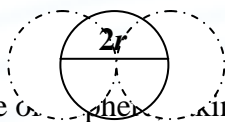
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**1.47.** In Section 1.13 it was stated that the van der Waals constant  $b$  is approximately four times the volume occupied by the molecules themselves. Justify this relationship for a gas composed of spherical molecules.

**Solution:**

The Van der Waals constant  $b$  represents the excluded volume occupied by the volume of the colliding molecules. When two molecules collide, the closest they can come to one another is a distance of  $2r$ , therefore the excluded volume per molecule can be represented as a sphere with a radius of no less than  $2r$ .



$b$  can be calculated using the volume of a sphere having the radius as  $2r$ .

$$V = \frac{4\pi r^3}{3}$$

where  $r = 2r$

$$V = \frac{4\pi (2r)^3}{3}$$

$$V = \frac{4\pi (8r^3)}{3} = 8V$$

$$b = 4V$$

Since we only consider the volume occupied by one molecule of radius  $r$ ,  $b=4V$ .

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**1.48.** Draw the van der Waals  $PV$  isotherm over the same range of  $P$  and  $V$  as in Figure 1.21 at 350 K and 450 K for  $\text{Cl}_2$  using the values in Table 1.4.

**Solution:**

Given: Figure 1.21  $T=350\text{K}$ ,  $T=450\text{K}$

Required: draw the Van der Waals isotherms

The curves are similar to those in Figure 1.21

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**1.49.** Compare the pressures predicted for  $0.8 \text{ dm}^3$  of  $\text{Cl}_2$  weighing  $17.5 \text{ g}$  at  $273.15 \text{ K}$  using (a) the ideal gas equation and (b) the van der Waals equation.

**Solution:**

Given:  $V = 0.8 \text{ dm}^3$ ,  $m_{\text{Cl}_2} = 17.5 \text{ g}$ ,  $T = 273.15 \text{ K}$

Required:  $P_{\text{Ideal}}$  and  $P_{\text{vdw}}$

From the ideal gas equation;  $P_{\text{Ideal}} = \frac{nRT}{V}$

$$P_{\text{Ideal}} = \frac{mRT}{MV}, \text{ where } n = \frac{m}{M}$$

Solving for  $P_{\text{Ideal}}$  yields;

$$P_{\text{Ideal}} = \frac{(17.5 \cancel{\text{g}})(8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}})(273.15 \cancel{\text{K}})}{(2 \times 35.4527 \cancel{\text{g mol}^{-1}})(0.8 \cancel{\text{dm}^3} \times 10^{-3} \text{ m}^3 \cancel{\text{dm}^{-3}})}$$

$$P_{\text{Ideal}} = 700\,658 \text{ J m}^{-3}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$P_{\text{Ideal}} = 700\,658 \text{ kg m}^2 \text{ s}^{-2} \text{ m}^{-3}$$

$$P_{\text{Ideal}} = 700\,658 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$\boxed{P_{\text{Ideal}} = 700.7 \text{ Pa}}$$

Using the van der Waals equation;  $P_{\text{vdw}} = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$

$$P_{\text{vdw}} = \frac{mRT}{M \left( V - \frac{m}{M} b \right)} - \frac{am^2}{M^2 V^2}, \text{ where } n = \frac{m}{M}$$

Solving for  $P_{\text{vdw}}$  with  $a = 0.6579 \text{ Pa m}^6 \text{ mol}^{-2}$  and  $b = 0.0562 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$  we get;

$$P_{\text{vdw}} = \frac{(17.5 \cancel{\text{g}})(8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}})(273.15 \cancel{\text{K}})}{(2 \times 35.4527 \cancel{\text{g mol}^{-1}}) \left( 0.8 \cancel{\text{dm}^3} \times 10^{-3} \text{ m}^3 \cancel{\text{dm}^{-3}} - \frac{(17.5 \cancel{\text{g}})}{(2 \times 35.4527 \cancel{\text{g mol}^{-1}})} (0.0562 \times 10^{-3} \text{ m}^3 \cancel{\text{mol}^{-1}}) \right)}$$

$$- \frac{(0.6579 \text{ Pa m}^6 \text{ mol}^{-2})(17.5 \cancel{\text{g}})^2}{(2 \times 35.4527 \cancel{\text{g mol}^{-1}})^2 (0.8 \cancel{\text{dm}^3} \times 10^{-3} \text{ m}^3 \cancel{\text{dm}^{-3}})^2}$$

$$P_{\text{vdw}} = 712\,997.84 \text{ Pa} - 62\,613.823\,3 \text{ Pa}$$

$$P_{\text{vdw}} = 650\,384.016\,7 \text{ Pa}$$

$$\boxed{P_{\text{vdw}} = 650 \text{ kPa}}$$

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- 1.50.** A particular mass of  $N_2$  occupies a volume of 1.00 L at  $-50^\circ\text{C}$  and 800 bar. Determine the volume occupied by the same mass of  $N_2$  at  $100^\circ\text{C}$  and 200 bar using the compressibility factor for  $N_2$ . At  $-50^\circ\text{C}$  and 800 bar it is 1.95; at  $100^\circ\text{C}$  and 200 bar it is 1.10. Compare this value to that obtained from the ideal gas law.

**Solution:**

Given:  $V_1 = 1.00\text{L}$ ,  $T_1 = -50^\circ\text{C} = 223.15\text{ K}$ ,  $P_1 = 800\text{ bar}$ ,  $Z_1 = 1.95$

$T_2 = 100^\circ\text{C} = 373.15\text{ K}$ ,  $P_2 = 200\text{ bar}$ ,  $Z_2 = 1.10$

Required:  $V_2$  and compare to  $V_{\text{ideal}}$

To determine  $V_2$ , we can use Eq. 1.98 for a real gas and rearrange for  $n$ , the number of moles of  $N_2$ :

$$Z = \frac{PV}{nRT}$$

$$n = \frac{ZPV}{RT}$$

The number of moles at  $V_2$  is the same as the number of moles at  $V_1$  since we know that the same mass is used.

$$n_1 = \frac{Z_1 P_1 V_1}{RT_1}, n_2 = \frac{Z_2 P_2 V_2}{RT_2}$$

where  $n_1 = n_2$ ,

$$\frac{Z_1 P_1 V_1}{RT_1} = \frac{Z_2 P_2 V_2}{RT_2}$$

Solving for  $V_2$  to get;

$$V_2 = \frac{Z_1 P_1 V_1 T_2}{Z_2 P_2 T_1}$$

$$V_2 = \frac{(1.95)(800\text{ bar})(1.00\text{ L})(223.15\text{ K})}{(1.10)(200\text{ bar})(373.15\text{ K})}$$

$$V_2 = 3.7747\text{ L}$$

$$\boxed{V_2 = 3.77\text{ L}}$$

To determine  $V_{\text{ideal}}$ , we can use Eq. 1.98 for an ideal gas, with  $Z = 1$  and rearrange for  $n$ , the number of moles of  $N_2$ ;

$$Z = \frac{PV}{nRT}, Z = 1$$

$$n = \frac{PV}{RT}$$

$$n_1 = \frac{P_1 V_1}{RT_1}, n_2 = \frac{P_2 V_{\text{ideal}}}{RT_2}$$

where  $n_1 = n_2$ ,

$$\frac{P_1 V_1}{RT_1} = \frac{P_2 V_{\text{ideal}}}{RT_2}$$

Now solving for  $V_{\text{ideal}}$ ;

$$V_{\text{ideal}} = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_{\text{ideal}} = \frac{(800 \text{ bar})(1.00 \text{ L})(223.15 \text{ K})}{(200 \text{ bar})(373.15 \text{ K})}$$

$$V_{\text{ideal}} = 6.68877 \text{ L}$$

$$\boxed{V_{\text{ideal}} = 6.69 \text{ L}}$$

We can now compare  $V_2$  and  $V_{\text{ideal}}$  by determining the error on  $V_{\text{ideal}}$ .

$$\text{error} = \frac{V_{\text{ideal}} - V_2}{V_2} \times 100\%$$

$$\text{error} = \frac{6.69 - 3.77}{3.77} \times 100\%$$

$$\text{error} = 0.7745 \times 100\%$$

$$\boxed{\text{error} = 77.5\%}$$

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**1.51.** A gas is found to obey the equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{V}$$

where  $a$  and  $b$  are constants not equal to zero. Determine whether this gas has a critical point; if it does, express the critical constants in terms of  $a$  and  $b$ . If it does not, explain how you determined this and the implications for the statement of the problem.

**Solution:**

Given:  $P = \frac{RT}{V-b} - \frac{a}{V}$  where  $a$  and  $b$  are constants not equal to zero

Required: critical point in terms of  $a$  and  $b$ , if it exists

According to Eq. 1.99, a gas has a critical point if  $\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$  and  $\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = -\frac{RT}{(V-b)^2} + \frac{a}{V^2} = 0$$

$$\frac{a}{V^2} = \frac{RT}{(V-b)^2} \quad (1)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = \frac{2RT}{(V-b)^3} - \frac{2a}{V^3} = 0$$

$$\frac{2a}{V^3} = \frac{2RT}{(V-b)^3} \quad (2)$$

If  $\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$  and  $\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$ , then  $\frac{(2)}{(1)}$  should not exist.

$$\frac{\left(\frac{2a}{V^3}\right)}{\left(\frac{a}{V^2}\right)} = \frac{\left(\frac{2RT}{(V-b)^3}\right)}{\left(\frac{RT}{(V-b)^2}\right)}$$

$$\frac{2V^2}{V^3} = \frac{2(V-b)^2}{(V-b)^3}$$

$$\frac{2}{V} = \frac{2}{V-b}$$

$$\frac{1}{V} = \frac{1}{V-b}$$

This last line  $\frac{1}{V} = \frac{1}{V-b}$  is only true if  $b = 0$ , however  $b \neq 0$  from the statement of the problem. Therefore the gas does not have a critical point.

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**1.52.** Ethylene ( $\text{C}_2\text{H}_4$ ) has a critical pressure of  $P_c = 61.659$  atm and a critical temperature of  $T_c = 308.6$  K. Calculate the molar volume of the gas at  $T = 97.2$  °C and 90.0 atm using Figure 1.22. Compare the value so found with that calculated from the ideal gas equation.

**Solution:**

Given: Ethylene ( $\text{C}_2\text{H}_4$ ): Figure 1.22,  $P_c = 61.659$  atm,  $T_c = 308.6$  K,  $P = 90.0$  atm,

$$T = 97.2\text{ °C} = 370.35\text{ K}$$

Required:  $V_m$ , and  $V_{\text{ideal}}$

First the reduced temperature and pressure of the gas can be obtained using the following ratios;  $T_r = \frac{T}{T_c}$  and  $P_r = \frac{P}{P_c}$

$$T_r = \frac{308.6\cancel{\text{K}}}{370.35\cancel{\text{K}}} = 1.20$$

$$P_r = \frac{90.0\cancel{\text{atm}}}{61.659\cancel{\text{atm}}} = 1.46$$

Using Figure 1.22, the compressibility factor for a gas of  $T_r = 1.20$  and  $P_r = 1.46$  is found to be approximately 0.7. Eq. 1.98 gives the compressibility in terms of molar volume. Rearranging this expression for  $V_m$  will allow us to calculate the molar volume.

$$Z = \frac{PV_m}{RT}$$

$$V_m = \frac{ZRT}{P}$$

$$V_m = \frac{0.7 \left( 0.08206\cancel{\text{atm dm}^3 \text{K}^{-1} \text{mol}^{-1}} \right) (370.35\cancel{\text{K}})}{(90.0\cancel{\text{atm}})}$$

$$V_m = 0.23637 \text{ dm}^3 \text{ mol}^{-1}$$

$$\boxed{V_m = 0.236 \text{ dm}^3 \text{ mol}^{-1}}$$

The molar volume obtained from the ideal gas equation is given by;

$$\frac{V}{n} = \frac{RT}{P} = V_m$$

$$V_m = \frac{RT}{P}$$

$$V_m = \frac{(0.08206 \cancel{\text{atm}} \text{ dm}^3 \cancel{\text{K}}^{-1} \text{ mol}^{-1})(370.35 \cancel{\text{K}})}{(90.0 \cancel{\text{atm}})}$$

$$V_m = 0.33767 \text{ dm}^3 \text{ mol}^{-1}$$

$$\boxed{V_m = 0.338 \text{ dm}^3 \text{ mol}^{-1}}$$

A comparison with the ideal molar volume shows that the real molar volume obtained from the law of corresponding states is much smaller.

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**1.53.** Assuming that methane is a perfectly spherical molecule, find the radius of one methane molecule using the value of  $b$  listed in Table 1.5.

**Solution:**

Given: methane ( $\text{CH}_4$ ): Table 1.5

Required:  $r_{\text{CH}_4}$

Using Table 1.5,  $b = 0.0428 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$  and  $b = 4V_m$ , as stated in section 1.13, the volume of methane is treated as a sphere;

$$V_{\text{CH}_4} = \frac{4\pi r^3}{3}$$

$$V_{\text{CH}_4} = \frac{b}{4L} = \frac{4\pi r^3}{3}$$

We can divide by  $L$ , Avogadro's number, since we are considering only one molecule of methane.

$$r = \sqrt[3]{\frac{b}{4L} \times \frac{3}{4\pi}}$$

$$r = \sqrt[3]{\frac{3}{16\pi} \times \frac{(0.0428 \times 10^{-3} \text{ m}^3 \cancel{\text{mol}^{-1}})}{(6.022 \times 10^{23} \cancel{\text{mol}^{-1}})}}$$

$$r = 1.61877 \times 10^{-10} \text{ m}$$

$$\boxed{r = 1.62 \times 10^{-10} \text{ m}}$$

The actual radius, i.e. the C-H distance in  $\text{CH}_4$  is  $1.09 \times 10^{-10} \text{ m}$ .

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**1.54.** Determine the Boyle temperature in terms of constants for the equation of state:

$$PV_m = RT\{1 + 8/57(P/P_c)(T_c/T)[1 - 4(T_c/T)^2]\}$$

$R$ ,  $P_c$ , and  $T_c$  are constants.

**Solution:**

$$\text{Given: } PV_m = RT\left\{1 + \frac{8}{57}\left(\frac{P}{P_c}\right)\left(\frac{T_c}{T}\right)\left[1 - 4\left(\frac{T_c}{T}\right)^2\right]\right\}$$

Required:  $T_B$ , Boyle temperature

The Boyle Temperature occurs when the second virial coefficient,  $B(T) = 0$  and the partial derivative  $\left(\frac{\partial(PV)}{\partial P}\right)_T$  becomes zero as  $P \rightarrow 0$ .

This is fulfilled when  $1 - 4\left(\frac{T_c}{T}\right)^2 = 0$ , therefore;

$$1 - 4\left(\frac{T_c}{T_B}\right)^2 = 0$$

$$\left(\frac{T_c}{T_B}\right)^2 = \frac{1}{4}$$

$$\frac{T_c}{T_B} = \frac{1}{2}$$

$$\boxed{T_B = 2T_c}$$

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**1.55.** Establish the relationships between van der Waals parameters  $a$  and  $b$  and the virial coefficients  $B$  and  $C$  of Eq. 1.117 by performing the following steps:

**a.** Starting with Eq. 1.101, show that

$$\frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT} \frac{1}{V_m}.$$

**b.** Since  $V_m/(V_m - b) = (1 - b/V_m)^{-1}$ , and  $(1 - x)^{-1} = 1 + x + x^2 + \dots$ , expand  $(1 - b/V_m)^{-1}$  to the quadratic term and substitute into the result of part (a).

**c.** Group terms containing the same power of  $V_m$  and compare to Eq. 1.117 for the case  $n = 1$ .

**d.** What is the expression for the Boyle temperature in terms of van der Waals parameters?

**Solution:**

Starting with equation 1.101  $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ , we can multiply by  $\frac{V_m}{RT}$  to get;

$$\frac{PV_m}{RT} = \left( \frac{V_m}{\cancel{RT}} \right) \frac{\cancel{RT}}{V_m - b} - \left( \frac{V_m}{RT} \right) \frac{a}{V_m^2}$$

$$\boxed{\frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT} \frac{1}{V_m}}$$

Since  $V_m/(V_m - b) = (1 - b/V_m)^{-1}$ , and  $(1 - x)^{-1} = 1 + x + x^2 + \dots$ , therefore we can write;

$$\left( 1 - \frac{b}{V_m} \right)^{-1} = 1 + \frac{b}{V_m} + \left( \frac{b}{V_m} \right)^2 + \dots$$

Using the expression derived above;

$$\frac{PV_m}{RT} = 1 + \frac{b}{V_m} + \left( \frac{b}{V_m} \right)^2 + \dots - \frac{a}{RT} \frac{1}{V_m}$$

Grouping the terms containing the same power of  $V_m$  gives;

$$\frac{PV_m}{RT} = 1 + \frac{1}{V_m} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{V_m} \right)^2 + \dots$$

Equation 1.117 is  $\frac{PV}{nRT} = 1 + \frac{B(T)n}{V} + \frac{C(T)n^2}{V^2} + \frac{D(T)n^4}{V^4} + \dots$ . For the case  $n = 1$ , this becomes,

$$\frac{PV_m}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^4} + \dots$$

Comparing to the expression we obtained in part c, we can see that:  $B(T) = \left( b - \frac{a}{RT} \right)$ ,  $C(T) = b^2$  and  $D(T) = 0$

The expression for the Boyle temperature in terms of van der Waals parameters is determined when  $B(T) = 0$ ;

$$\left( b - \frac{a}{RT_B} \right) = 0$$

$$b = \frac{a}{RT_B}$$

$$\boxed{T_B = \frac{a}{bR}}$$

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**1.56.** Determine the Boyle temperature of a van der Waals gas in terms of the constants  $a$ ,  $b$ , and  $R$ .

**Solution:**

Given: A van der Waals gas

Required:  $T_B$  of the constants  $a$ ,  $b$ , and  $R$

The temperature can be obtained by rearranging the van der Waals equation;

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad (\text{Eq. 1.100})$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

We can then multiply through by  $\frac{V}{RT}$  to change the form of the equation;

$$\frac{PV}{RT} = \left( \frac{V}{\cancel{RT}} \right) \frac{\cancel{RT}}{V - b} - \left( \frac{\cancel{V}}{RT} \right) \frac{a}{V^{\cancel{2}}}$$

$$\frac{PV}{RT} = \frac{V}{V - b} - \frac{a}{RTV}$$

$$Z = \frac{V}{V - b} - \frac{a}{RTV}$$

Since  $V/(V-b) = (1 - b/V)^{-1}$ , and  $(1-x)^{-1} = 1 + x + x^2 + \dots$ , therefore;

$$\left(1 - \frac{b}{V}\right)^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \dots$$

$$Z = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \dots - \frac{a}{RT} \frac{1}{V}$$

Grouping the terms containing the same power of  $V$  gives,

$$Z = 1 + \frac{1}{V} \left( b - \frac{a}{RT} \right) + \left(\frac{b}{V}\right)^2 + \dots$$

The Boyle Temperature occurs when the second virial coefficient,  $B(T) = 0$  and the partial derivative  $\left(\frac{\partial Z}{\partial P}\right)_T$  becomes zero as  $P \rightarrow 0$ , i.e.:

$$\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P}\right)_T = 0$$

By changing the variable  $V$  into  $\frac{RT}{P}$  we can get;



$$Z = 1 + \frac{P}{RT} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{RT} \right)^2 P^2 + \dots$$

$$\left( \frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left( b - \frac{a}{RT} \right) + 2 \left( \frac{b}{RT} \right)^2 P$$

$$\lim_{P \rightarrow 0} \left( \frac{\partial Z}{\partial P} \right)_T = 0$$

$$\lim_{P \rightarrow 0} \left( \frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left( b - \frac{a}{RT} \right) = 0$$

where  $B(T) = 0$

$$B(T_B) = 0 = \frac{1}{RT_B} \left( b - \frac{a}{RT_B} \right)$$

$$b - \frac{a}{RT_B} = 0$$

$$b = \frac{a}{RT_B}$$

$$\boxed{T_B = \frac{a}{Rb}}$$

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**1.57.** The critical temperature  $T_c$  of nitrous oxide ( $\text{N}_2\text{O}$ ) is  $36.5^\circ\text{C}$ , and its critical pressure  $P_c$  is  $71.7\text{ atm}$ . Suppose that  $1\text{ mol}$  of  $\text{N}_2\text{O}$  is compressed to  $54.0\text{ atm}$  at  $356\text{ K}$ . Calculate the reduced temperature and pressure, and use Figure 1.22, interpolating as necessary, to estimate the volume occupied by  $1\text{ mol}$  of the gas at  $54.0\text{ atm}$  and  $356\text{ K}$ .

**Solution:**

The reduced temperature and pressure of the gas can be obtained using the ratios  $T_r = \frac{T}{T_c}$  and  $P_r = \frac{P}{P_c}$

Using the values above, we obtain

$$T_r = \frac{356\text{ K}}{(273.15 + 36.5)\text{ K}}$$

$$T_r = 1.149\,69$$

$$\boxed{T_r = 1.15}$$

$$P_r = \frac{54.0\text{ atm}}{71.7\text{ atm}}$$

$$P_r = 0.753\,138$$

$$\boxed{P_r = 0.753}$$

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**1.58.** At what temperature and pressure will  $\text{H}_2$  be in a corresponding state with  $\text{CH}_4$  at 500.0 K and 2.00 bar pressure? Given  $T_c = 33.2$  K for  $\text{H}_2$ , 190.6 K for  $\text{CH}_4$ ;  $P_c = 13.0$  bar for  $\text{H}_2$ , 46.0 bar for  $\text{CH}_4$ .

**Solution:**

Given:  $T_{\text{CH}_4} = 500.0$  K,  $P_{\text{CH}_4} = 2.00$  bar,  $T_{c_{\text{H}_2}} = 33.2$  K,

$T_{c_{\text{CH}_4}} = 190.6$  K,  $P_{c_{\text{H}_2}} = 13.0$  bar,  $P_{c_{\text{CH}_4}} = 46.0$  bar

Required:  $T_{\text{H}_2}$  and  $P_{\text{H}_2}$

In order for hydrogen to be in the corresponding state as methane, they must have the same reduced temperature and reduced pressure. The reduced temperature and pressure of the gas can be obtained using the ratios  $T_r = \frac{T}{T_c}$  and  $P_r = \frac{P}{P_c}$

$$T_r = \frac{T_{\text{CH}_4}}{T_{c_{\text{CH}_4}}}$$

$$T_r = \frac{500.0 \cancel{\text{K}}}{190.6 \cancel{\text{K}}}$$

$$T_r = 2.623$$

$$P_r = \frac{P_{\text{CH}_4}}{P_{c_{\text{CH}_4}}}$$

$$P_r = \frac{2.00 \cancel{\text{bar}}}{46.0 \cancel{\text{bar}}}$$

$$P_r = 4.35 \times 10^{-2}$$

$T_{\text{H}_2}$  and  $P_{\text{H}_2}$  are given by rearranging the ratios for reduced temperature and pressure.

$$T_{\text{H}_2} = T_r T_{c_{\text{H}_2}} \quad \text{and} \quad P_{\text{H}_2} = P_r P_{c_{\text{H}_2}}$$

Solving for  $T_{\text{H}_2}$  and  $P_{\text{H}_2}$  gives;

$$T_{\text{H}_2} = (2.623)(33.2 \text{ K})$$

$$T_{\text{H}_2} = 87.0836 \text{ K}$$

$$P_{\text{H}_2} = (4.35 \times 10^{-2})(13.0 \text{ bar})$$

$$P_{\text{H}_2} = 0.5655 \text{ bar}$$

$$T_r = \frac{T_{\text{CH}_4}}{T_{c_{\text{CH}_4}}}$$

$$T_r = \frac{500.0 \cancel{\text{K}}}{190.6 \cancel{\text{K}}}$$

$$T_r = 2.623$$

$$P_r = \frac{P_{\text{CH}_4}}{P_{c_{\text{CH}_4}}}$$

$$P_r = \frac{2.00 \cancel{\text{bar}}}{46.0 \cancel{\text{bar}}}$$

$$P_r = 4.35 \times 10^{-2}$$

$$T_{c_{\text{H}_2}} = 33.2 \text{ K}$$

$$P_{c_{\text{H}_2}} = 13.0 \text{ bar}$$

$$T_{\text{H}_2} = 87.1 \text{ K}$$

$$P_{\text{H}_2} = 0.566 \text{ bar}$$

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**1.59.** For the Dieterici equation, derive the relationship of  $a$  and  $b$  to the critical volume and temperature.

[Hint: Remember that at the critical point  $(\partial P/\partial V)_T = 0$  and  $(\partial^2 P/\partial V^2)_T = 0$ .]

**Solution:**

Given: Dieterici equation:  $(Pe^{a/V_m RT})(V_m - b) = RT$

Required: The relationship of  $a$  and  $b$  to  $V_c$  and  $T_c$

By rearranging for  $P$  and using Eq.1.114,  $(\partial P/\partial V)_T$  and  $(\partial^2 P/\partial V^2)_T$  can be determined.

$$P = \frac{RT}{(V_m - b)} e^{-a/V_m RT}$$

$$\left( \frac{\partial P}{\partial V_m} \right)_T = -\frac{RT}{(V_m - b)^2} e^{-a/V_m RT} + \left( -\frac{a}{RT} \left( -\frac{1}{V_m^2} \right) \right) e^{-a/V_m RT} \frac{RT}{(V_m - b)}$$

$$\left( \frac{\partial P}{\partial V_m} \right)_T = \frac{RT}{(V_m - b)} e^{-a/V_m RT} \left( \frac{a}{RTV_m^2} - \frac{1}{(V_m - b)} \right)$$

$$\left( \frac{\partial P}{\partial V_m} \right)_T = P \left( \frac{a}{RTV_m^2} - \frac{1}{(V_m - b)} \right)$$

$$\left( \frac{\partial^2 P}{\partial V_m^2} \right)_T = \left( \frac{\partial P}{\partial V_m} \right)_T \left( \frac{a}{RTV_m^2} - \frac{1}{(V_m - b)} \right) + \left( -\frac{2a}{RTV_m^3} + \frac{1}{(V_m - b)^2} \right) P$$

$$\left( \frac{\partial^2 P}{\partial V_m^2} \right)_T = P \left( \frac{a}{RTV_m^2} - \frac{1}{(V_m - b)} \right)^2 + P \left( -\frac{2a}{RTV_m^3} + \frac{1}{(V_m - b)^2} \right)$$

$$\left( \frac{\partial^2 P}{\partial V_m^2} \right)_T = P \left[ \left( \frac{a}{RTV_m^2} - \frac{1}{(V_m - b)} \right)^2 - \frac{2a}{RTV_m^3} + \frac{1}{(V_m - b)^2} \right]$$

Solving for  $(\partial P/\partial V)_T = 0$  and  $(\partial^2 P/\partial V^2)_T = 0$ , the condition of the critical point, The relationship of  $a$  and  $b$  to  $V_c$  and  $T_c$  can then be obtained;

$$\left(\frac{\partial P}{\partial V_m}\right)_{T_c} = P \left( \frac{a}{RTV_m^2} - \frac{1}{(V_m - b)} \right) = 0$$

$$P \left( \frac{a}{RT_c V_c^2} - \frac{1}{(V_c - b)} \right) = 0$$

$$a = \frac{RT_c V_c^2}{(V_c - b)}$$

$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = P \left[ \left( \frac{a}{RTV_m^2} - \frac{1}{(V_m - b)} \right)^2 - \frac{2a}{RTV_m^3} + \frac{1}{(V_m - b)^2} \right] = 0$$

$$P \left[ \left( \frac{a}{RT_c V_c^2} - \frac{1}{(V_c - b)} \right)^2 - \frac{2a}{RT_c V_c^3} + \frac{1}{(V_c - b)^2} \right] = 0$$

$$\left( \frac{a}{RT_c V_c^2} - \frac{1}{(V_c - b)} \right)^2 - \frac{2a}{RT_c V_c^3} + \frac{1}{(V_c - b)^2} = 0$$

Substituting the expression for  $a$  into the above can further simplify the problem;

$$\left( \frac{1}{\cancel{RT_c V_c^2}} \left( \frac{\cancel{RT_c V_c^2}}{(V_c - b)} \right) - \frac{1}{(V_c - b)} \right)^2 - \frac{2}{\cancel{RT_c V_c^2}} \left( \frac{\cancel{RT_c V_c^2}}{(V_c - b)} \right) + \frac{1}{(V_c - b)^2} = 0$$

$$\left( \frac{1}{(V_c - b)} - \frac{1}{(V_c - b)} \right)^2 - \frac{2}{V_c (V_c - b)} + \frac{1}{(V_c - b)^2} = 0$$

$$\frac{2}{V_c} = \frac{1}{(V_c - b)}$$

$$2(V_c - b) = V_c$$

$$b = V_c - \frac{V_c}{2}$$

$$b = \frac{V_c}{2}$$

The Dieterici constant  $a$  then becomes,

$$a = \frac{RT_c V_c^2}{\left( V_c - \frac{V_c}{2} \right)}$$

$$a = \frac{RT_c V_c^2}{\left( \frac{V_c}{2} \right)}$$

$$a = 2RT_c V_c$$

Substitution back into the Dieterici equation, the critical point becomes,

$$P = \frac{RT}{(V_m - b)} e^{-a/V_m RT}, \quad a = 2RT_c V_c \quad \text{and} \quad b = \frac{V_c}{2}$$

$$P_c = \frac{RT_c}{\left(V_c - \frac{V_c}{2}\right)} e^{-\frac{2RT_c}{V_c RT_c}}$$

$$P_c = \frac{RT_c}{\left(\frac{V_c}{2}\right)} e^{-2}$$

$$\boxed{P_c = \frac{2RT_c}{V_c} e^{-2}}$$

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**1.60.** In Eq. 1.103 a cubic equation has to be solved in order to find the volume of a van der Waals gas. However, reasonably accurate estimates of volumes can be made by deriving an expression for the compression factor  $Z$  in terms of  $P$  from the result of the previous problem. One simply substitutes for the terms  $V_m$  on the right-hand side in terms of the ideal gas law expression  $V_m = RT/P$ . Derive this expression and use it to find the volume of  $\text{CCl}_2\text{F}_2$  at  $30.0^\circ\text{C}$  and  $5.00$  bar pressure. What will be the molar volume computed using the ideal gas law under the same conditions?

**Solution:**

Given: (from problem 1.59):  $\text{CCl}_2\text{F}_2$  at  $T = 30.0^\circ\text{C} = 303.15\text{ K}$  and  $P = 5.00$  bar

Required:  $V_m$  and  $V_{m,\text{ideal}}$

The compression factor ;  $Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$  can be used with Eq. 1.101 to obtain an expression for  $Z$ ;

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$Z = \frac{PV_m}{RT} = \left( \frac{V_m}{RT} \right) \frac{RT}{V_m - b} - \left( \frac{V_m}{RT} \right) \frac{a}{V_m^2}$$

$$Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$$

Since  $V_m/(V_m - b) = (1 - b/V_m)^{-1}$ , and  $(1 - x)^{-1} = 1 + x + x^2 + \dots$ , therefore;

$$\left( 1 - \frac{b}{V_m} \right)^{-1} = 1 + \frac{b}{V_m} + \left( \frac{b}{V_m} \right)^2 + \dots$$

$$Z = 1 + \frac{b}{V_m} + \left( \frac{b}{V_m} \right)^2 + \dots - \frac{a}{RT} \frac{1}{V_m}$$

$$Z = 1 + \frac{1}{V_m} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{V_m} \right)^2 + \dots$$

Using  $V_m = RT/P$ , we obtain;

$$Z = 1 + \frac{P}{RT} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{RT} \right) P^2$$

Table 1.5 gives the van der Waals constants for  $\text{CCl}_2\text{F}_2$  :

$$a = 1.066 \text{ dm}^3 \text{ bar mol}^{-2}, b = 0.0973 \text{ dm}^3 \text{ mol}^{-1}$$

$$Z = 1 + \frac{(5.00 \text{ bar})}{(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})} \times$$

$$\left( 0.0973 \text{ dm}^3 \text{ mol}^{-1} - \frac{1.066 \text{ dm}^3 \text{ bar mol}^{-2}}{(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})} \right)$$

$$+ \left( \frac{0.0973 \text{ dm}^3 \text{ mol}^{-1}}{(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})} \right)^2 (5.00 \text{ bar})^2$$

$$Z = 1.01167$$

$$Z = 1.01$$

We can then solve for  $V_m$  by rearranging the expression for the compression factor;

$$Z = \frac{PV_m}{RT}$$

$$V_m = \frac{ZRT}{P}$$

$$V_m = \frac{1.01(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})}{(5.00 \text{ bar})}$$

$$V_m = 5.0918 \text{ dm}^3 \text{ mol}^{-1}$$

$$\boxed{V_m = 5.09 \text{ dm}^3 \text{ mol}^{-1}}$$

$V_{m_{\text{ideal}}}$  can also be obtained using the ideal gas,  $PV = nRT$ , and solving for  $V_m$ ,

$$V_{m_{\text{ideal}}} = \frac{RT}{P}$$
$$V_{m_{\text{ideal}}} = \frac{(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})}{(5.00 \text{ bar})}$$

$$V_{m_{\text{ideal}}} = 5.04138 \text{ dm}^3 \text{ mol}^{-1}$$

$$\boxed{V_{m_{\text{ideal}}} = 5.04 \text{ dm}^3 \text{ mol}^{-1}}$$

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**1.61.** A general requirement of all equations of state for gases is that they reduce to the ideal gas equation (Eq. 1.28) in the limit of low pressures. Show that this is true for the van der Waals equation.

**Solution:**

Given:  $PV = nRT$ , low  $P$

Required: show that the van der Waals equation reduces to Eq. 1.28

The Van der Waals equation is given by;

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (\text{Eq. 1.100})$$

Using the compression factor,  $Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$ , Eq. 1.100 can be recast in a form of  $Z$  in terms of  $P$ .

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$Z = \frac{PV_m}{RT} = \left(\frac{V_m}{RT}\right) \frac{RT}{V_m - b} - \left(\frac{V_m}{RT}\right) \frac{a}{V_m^2}$$

$$Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$$

Since  $V_m/(V_m - b) = (1 - b/V_m)^{-1}$ , and  $(1 - x)^{-1} = 1 + x + x^2 + \dots$ , therefore;

$$\left(1 - \frac{b}{V_m}\right)^{-1} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \dots$$

$$Z = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \dots - \frac{a}{RT} \frac{1}{V_m}$$

$$Z = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT}\right) + \left(\frac{b}{V_m}\right)^2 + \dots$$

Using  $V_m = RT/P$  we obtain;

$$Z = 1 + \frac{P}{RT} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{RT} \right) P^2$$

Taking the limit of  $Z$  as  $P$  approaches 0 becomes,

$$\lim_{P \rightarrow 0} \left( 1 + \frac{P}{RT} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{RT} \right) P^2 \right)$$

$$\lim_{P \rightarrow 0} = 1$$

$$\boxed{Z = 1}$$

Which is true for an ideal gas, and therefore the van der Waals equation reduces to the ideal gas equation.

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**1.62.** The van der Waals constants for  $\text{C}_2\text{H}_6$  in the older literature are found to be

$$a = 5.49 \text{ atm L}^2 \text{ mol}^{-2} \text{ and } b = 0.0638 \text{ L mol}^{-1}$$

Express these constants in SI units ( $\text{L} = \text{liter} = \text{dm}^3$ ).

**Solution:**

Given:  $PV = nRT$ , low  $P$ ,  $a = 5.49 \text{ atm L}^2 \text{ mol}^{-2}$  and  $b = 0.0638 \text{ L mol}^{-1}$

Required: express  $a$  and  $b$  in SI units

$$1 \text{ atm} = 101\,325 \text{ Pa}$$

$$1 \text{ L}^2 = (1 \text{ dm})^6 = (0.1 \text{ m})^6 = 1 \times 10^{-6} \text{ m}^6$$

$$a = 5.49 \text{ atm L}^2 \text{ mol}^{-2} \times \frac{101\,325 \text{ Pa}}{1 \text{ atm}} \times \frac{1 \times 10^{-6} \text{ m}^6}{1 \text{ L}^2}$$

$$\boxed{a = 5.56 \times 10^{-1} \text{ Pa m}^6 \text{ mol}^{-2}}$$

$$1 \text{ L} = (1 \text{ dm})^3 = (0.1 \text{ m})^3 = 1 \times 10^{-3} \text{ m}^3$$

$$b = 0.0638 \text{ L mol}^{-1} \times \frac{1 \times 10^{-3} \text{ m}^3}{1 \text{ L}}$$

$$\boxed{b = 6.38 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

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**1.63.** Compare the values obtained for the pressure of 3.00 mol CO<sub>2</sub> at 298.15 K held in a 8.25-dm<sup>3</sup> bulb using the ideal gas, van der Waals, Dieterici, and Beattie-Bridgeman equations. For CO<sub>2</sub> the Dieterici equation constants are

$$a = 0.462 \text{ Pa m}^6 \text{ mol}^{-2},$$

$$b = 4.63 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

**Solution:**

Given:  $n = 3.00 \text{ mol}$ ,  $T_{\text{CO}_2} = 298.15 \text{ K}$ ,  $V_{\text{CO}_2} = 8.25 \text{ dm}^3$

$$a_{\text{Dieterici}} = 0.462 \text{ Pa m}^6 \text{ mol}^{-2}, \quad b_{\text{Dieterici}} = 4.63 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Required:  $P_{\text{ideal}}$ ,  $P_{\text{vdw}}$ ,  $P_{\text{Dieterici}}$  and  $P_{\text{BB}}$

The Ideal Gas equation is given by;

$$P_{\text{ideal}} = \frac{nRT}{V}$$

$$P_{\text{ideal}} = \frac{(3.00 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{\left(8.25 \text{ dm}^3 \times \frac{1 \times 10^{-3} \text{ m}^3}{1 \text{ dm}^3}\right)}$$

$$P_{\text{ideal}} = 901\,400 \text{ J m}^{-3}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ ,  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$P_{\text{ideal}} = 901\,400 \text{ kg m}^2 \text{ s}^{-2} \text{ m}^{-3}$$

$$P_{\text{ideal}} = 901\,400 \text{ Pa}$$

where  $1 \text{ bar} = 100\,000 \text{ Pa}$

$$\boxed{P_{\text{ideal}} = 9.01 \text{ bar}}$$

The Van der Waals equation is defined as;

$$P_{\text{vdw}} = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$V_m = \frac{V}{n} = \left( \frac{8.25 \text{ dm}^3}{1} \times \frac{1 \times 10^{-3} \text{ m}^3}{1 \text{ dm}^3} \right) \times \frac{1}{(3.00 \text{ mol})}$$

$$V_m = 2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

From Table 1.5,  $a = 0.3640 \text{ Pa m}^6 \text{ mol}^{-2}$ ,  $b = 0.0427 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$

$$P_{\text{vdw}} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}) - (0.0427 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})} - \frac{(0.3640 \text{ Pa m}^6 \text{ mol}^{-2})}{(2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})^2}$$

$$P_{\text{vdw}} = 915\,661 \text{ J m}^{-3} - 48\,132 \text{ Pa}$$

$$P_{\text{vdw}} = 915\,661 \text{ Pa} - 48\,132 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$P_{\text{vdw}} = 867\,528 \text{ Pa}$$

$$P_{\text{vdw}} = 8.68 \text{ bar}$$

The Dieterici Equation is as follows;

$$P_{\text{Dieterici}} = \frac{RT}{(V_m - b)} e^{-a/V_m RT}$$

$$a_{\text{Dieterici}} = 0.462 \text{ Pa m}^6 \text{ mol}^{-2}, b_{\text{Dieterici}} = 4.63 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}, V_m = 2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

$$P_{\text{Dieterici}} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}) - (4.63 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})} e^{-\frac{(0.462 \text{ Pa m}^6 \text{ mol}^{-2})}{(2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$P_{\text{Dieterici}} = 856\,801 \text{ Pa}$$

$$P_{\text{Dieterici}} = 8.57 \text{ bar}$$

The Beattie-Bridgeman equation;



$$P_{BB} = \frac{RT}{V_m^2} \left[ 1 - \left( \frac{c}{V_m T^3} \right) \right] (V_m + B) - \frac{A}{V_m^2}$$

$$\text{where } A = A_0 \left( 1 - \frac{a}{V_m} \right), B = B_0 \left( 1 - \frac{b}{V_m} \right)$$

From Table 1.6:

$$A_0 = 0.50728 \text{ Pa m}^6 \text{ mol}^{-2}, a = 71.32 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}, B_0 = 104.76 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}, b = 72.35 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}, c = 66.00 \times 10 \text{ m}^3 \text{ K}^3 \text{ mol}^{-1}$$

$$A = 0.50728 \text{ Pa m}^6 \text{ mol}^{-2} \left( 1 - \frac{71.32 \times 10^{-6} \cancel{\text{m}^3 \cancel{\text{mol}^{-1}}}}{2.75 \times 10^{-3} \cancel{\text{m}^3 \cancel{\text{mol}^{-1}}}} \right)$$

$$A = 0.494124 \text{ Pa m}^6 \text{ mol}^{-2}$$

$$B = (104.76 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \left( 1 - \frac{72.35 \times 10^{-6} \cancel{\text{m}^3 \cancel{\text{mol}^{-1}}}}{2.75 \times 10^{-3} \cancel{\text{m}^3 \cancel{\text{mol}^{-1}}}} \right)$$

$$B = 1.02004 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

Solving for  $P_{BB}$  gives,

$$P_{BB} = \frac{(8.3145 \text{ J } \cancel{\text{K}} \text{ mol}^{-1})(298.15 \cancel{\text{K}})}{(2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})^2} \left[ 1 - \left( \frac{66.00 \times 10 \cancel{\text{m}^3 \cancel{\text{K}^3 \cancel{\text{mol}^{-1}}}}{(2.75 \times 10^{-3} \cancel{\text{m}^3 \cancel{\text{mol}^{-1}}})(298.15 \cancel{\text{K}})^3} \right) \right]$$

$$\times (2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} + (1.02004 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})) - \frac{(0.013156 \text{ Pa m}^6 \text{ mol}^{-2})}{(2.75 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})^2}$$

$$P_{BB} = 861075 \text{ Pa}$$

$$\boxed{P_{BB} = 8.61 \text{ bar}}$$

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**1.64.** A gas obeys the van der Waals equation with  $P_c = 3.040 \times 10^6 \text{ Pa}$  ( $= 30 \text{ atm}$ ) and  $T_c = 473 \text{ K}$ . Calculate the value of the van der Waals constant  $b$  for this gas.

**Solution:**

Given:  $P_c = 3.040 \times 10^6 \text{ Pa}$  ( $= 30 \text{ atm}$ ) and  $T_c = 473 \text{ K}$

Required:  $b$

From Eq. 1.109;  $b = \frac{V_c}{3}$  and  $R = \frac{8P_c V_c}{3T_c}$

It is possible to rearrange the expression for the gas constant to express it in terms of  $V_c$ , so that we can isolate for  $b$ .

$$V_c = \frac{3RT_c}{8P_c}$$

$$b = \frac{1}{3} \frac{3RT_c}{8P_c}$$

$$b = \frac{RT_c}{8P_c}$$

$$b = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) 473 \text{ K}}{8(3.040 \times 10^6 \text{ Pa})}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ J}}{1 \text{ Pa}} = \frac{1 \text{ kg m}^2 \cancel{\text{s}^{-2}}}{1 \text{ kg m}^{-1} \cancel{\text{s}^{-2}}} = 1 \text{ m}^3$$

$$b = 1.61709 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

$$\boxed{b = 1.62 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}$$

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- 1.65.** Expand the Dieterici equation in powers of  $V_m^{-1}$  in order to cast it into the virial form. Find the second and third virial coefficients. Then show that at low densities the Dieterici and van der Waals equations give essentially the same result for  $P$ .

**Solution:**

Given:  $(Pe^{a/V_m RT})(V_m - b) = RT$

Required: second and third virial coefficients

First, the Dieterici equation can be rewritten in terms of  $P$  as;

$$P_{\text{Dieterici}} = \frac{RT}{(V_m - b)} e^{-a/V_m RT}$$

The series expansion for  $e^x$  is given by  $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$  can be used to expand the Dieterici equation.

$$P_{\text{Dieterici}} = \frac{RT}{(V_m - b)} \left\{ 1 + \left( \frac{-a}{V_m RT} \right) + \frac{\left( \frac{-a}{V_m RT} \right)^2}{2!} + \dots \right\}$$

$$P_{\text{Dieterici}} = \frac{RT}{(V_m - b)} + \left( \frac{RT}{(V_m - b)} \right) \left( \frac{-a}{V_m RT} \right) + \left( \frac{RT}{(V_m - b)} \right) \frac{\left( \frac{-a}{V_m RT} \right)^2}{2!} + \dots$$

$$P_{\text{Dieterici}} = \frac{RT}{(V_m - b)} - \frac{a}{V_m (V_m - b)} + \frac{a^2}{2RTV_m^2 (V_m - b)} - \dots$$

Expanding  $\frac{1}{V_m - b}$  and collecting terms in powers of  $V_m$  gives coefficients that are independent of  $V_m$  :

$$\frac{1}{V_m - b} = \frac{1}{V_m} \left( 1 - \frac{b}{V_m} \right)^{-1} = \frac{1}{V_m} \left( 1 - \frac{b}{V_m} + \left( \frac{b}{V_m} \right)^2 - \dots \right)$$

Substitution into the Dieterici equation leads to;

$$P = \frac{RT}{V_m} - \frac{a + RTb}{V_m^2} + \frac{1}{V_m^3} \left( \frac{a^2}{2RT} + ab + RTb^2 \right) - \dots$$

The second coefficient is  $-(a + RTb)$  and the third coefficient is  $\left( \frac{a^2}{2RT} + ab + RTb^2 \right)$ .

At low densities, the third and higher terms are negligible. Dropping the third and higher terms, and substituting, we obtain

$$P = \frac{RT}{V_m} - \frac{a + RTb}{V_m^2}$$

This is in the same form as the van der Waals equation.

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# CHAPTER 2 The First Law of Thermodynamics

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## Physical Chemistry

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## Problems and Solutions

## Chapter 2

*\*problems with an asterisk are slightly more demanding*

### Energy, Heat, and Work

- 2.1.** A bird weighing 1.5 kg leaves the ground and flies to a height of 75 metres, where it attains a velocity of  $20 \text{ m s}^{-1}$ . What change in energy is involved in the process? (Acceleration of gravity =  $9.81 \text{ m s}^{-2}$ .)

[Solution](#)

- 2.2.** The densities of ice and water at  $0^\circ\text{C}$  are  $0.9168$  and  $0.9998 \text{ g cm}^{-3}$ , respectively. If  $\Delta H$  for the fusion process at atmospheric pressure is  $6.025 \text{ kJ mol}^{-1}$ , what is  $\Delta U$ ? How much work is done on the system?

[Solution](#)

- 2.3.** The density of liquid water at  $100^\circ\text{C}$  is  $0.9584 \text{ g cm}^{-3}$ , and that of steam at the same temperature is  $0.000 596 \text{ g cm}^{-3}$ . If the enthalpy of evaporation of water at atmospheric pressure is  $40.63 \text{ kJ mol}^{-1}$ , what is  $\Delta U$ ? How much work is done by the system during the evaporation process?

[Solution](#)

- 2.4.** The latent heat of fusion of water at  $0^\circ\text{C}$  is  $6.025 \text{ kJ mol}^{-1}$  and the molar heat capacities ( $C_{P,m}$ ) of water and ice are  $75.3$  and  $37.7 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. The  $C_P$  values can be taken to be independent of temperature. Calculate  $\Delta H$  for the freezing of 1 mol of supercooled water at  $-10.0^\circ\text{C}$ .

[Solution](#)

- 2.5.** A sample of liquid acetone weighing  $0.700 \text{ g}$  was burned in a bomb calorimeter for which the heat capacity (including the sample) is  $6937 \text{ J K}^{-1}$ . The observed temperature rise was from  $25.00^\circ\text{C}$  to  $26.69^\circ\text{C}$ .
- Calculate  $\Delta U$  for the combustion of 1 mol of acetone.
  - Calculate  $\Delta H$  for the combustion of 1 mol of acetone.

[Solution](#)

- 2.6.** An average man weighs about 70 kg and produces about 10 460 kJ of heat per day.
- a.** Suppose that a man were an isolated system and that his heat capacity were  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ ; if his temperature were  $37^\circ\text{C}$  at a given time, what would be his temperature 24 h later?
- b.** A man is in fact an open system, and the main mechanism for maintaining his temperature constant is evaporation of water. If the enthalpy of vaporization of water at  $37^\circ\text{C}$  is  $43.4 \text{ kJ mol}^{-1}$ , how much water needs to be evaporated per day to keep the temperature constant?

[Solution](#)

- 2.7.** In an open beaker at  $25^\circ\text{C}$  and 1 atm pressure, 100 g of zinc are caused to react with dilute sulfuric acid. Calculate the work done by the liberated hydrogen gas, assuming it behaves ideally. What would be the work done if the reaction took place in a sealed vessel?

[Solution](#)

- 2.8.** A balloon is 0.50 m in diameter and contains air at  $25^\circ\text{C}$  and 1 bar pressure. It is then filled with air isothermally and reversibly until the pressure reaches 5 bar. Assume that the pressure is proportional to the diameter of the balloon and calculate (a) the final diameter of the balloon and (b) the work done in the process.

[Solution](#)

- 2.9.** When 1 cal of heat is given to 1 g of water at  $14.5^\circ\text{C}$ , the temperature rises to  $15.5^\circ\text{C}$ . Calculate the molar heat capacity of water at  $15^\circ\text{C}$ .

[Solution](#)

- 2.10.** A vessel containing 1.000 kg of water at  $25.00^\circ\text{C}$  is heated until it boils. How much heat is supplied? How long would it take a one-kilowatt heater to supply this amount of heat? Assume the heat capacity calculated in Problem 2.9 to apply over the temperature range.

[Solution](#)

- 2.11.** A nonporous ceramic of volume  $V \text{ m}^3$  and mass  $M \text{ kg}$  is immersed in a liquid of density  $d \text{ kg m}^{-3}$ . What is the work done on the ceramic if it is slowly raised a height  $h \text{ m}$  through the liquid? Neglect any resistance caused by viscosity. What is the change in the potential energy of the ceramic?

[Solution](#)

**2.12.** Show that the differential  $dP$  of the pressure of an ideal gas is an exact differential.

[Solution](#)

**2.13.** Determine whether  $dU = xy^2dx + x^2ydy$  is an exact differential. If it is find the function  $U$  of which  $dU$  is the differential. Do this by integrating over suitable paths. In a plot of  $y$  against  $x$ , show a plot of the paths that you chose.

[Solution](#)

### Thermochemistry

**2.14.** Using the data given in Table 2.1 and Appendix D, find the enthalpy change for the reaction  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$  at 800 K.

[Solution](#)

**2.15.** A sample of liquid benzene weighing 0.633 g is burned in a bomb calorimeter at 25.00 °C, and 26.54 kJ of heat are evolved.  
a. Calculate  $\Delta U$  per mole of benzene.  
b. Calculate  $\Delta H$  per mole of benzene.

[Solution](#)

**2.16.** Deduce the standard enthalpy change for the process  
$$2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$$
from the data in Appendix D.

[Solution](#)

**2.17.** A sample of liquid methanol weighing 5.27 g was burned in a bomb calorimeter at 25.00 °C, and 119.50 kJ of heat was evolved (after correction for standard conditions).  
a. Calculate  $\Delta_c H^\circ$  for the combustion of 1 mol of methanol.  
b. Use this value and the data in Appendix D for  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$  to obtain a value for  $\Delta_f H^\circ(\text{CH}_3\text{OH}, \text{l})$ , and compare with the value given in the table.  
c. If the enthalpy of vaporization of methanol is  $35.27 \text{ kJ mol}^{-1}$ , calculate  $\Delta_f H^\circ$  for  $\text{CH}_3\text{OH}(\text{g})$ .

[Solution](#)



**2.18.** Calculate the heat of combustion ( $\Delta_c H^\circ$ ) of ethane from the data given in Appendix D.

[Solution](#)

**2.19.** The model used to describe the temperature dependence of heat capacities (Eq. 2.48; Table 2.1) cannot remain valid as the temperature approaches absolute zero because of the  $1/T^2$  term. In some cases, the model starts to break down at temperatures significantly higher than absolute zero. The following data for nickel are taken from a very old textbook (*Numerical Problems in Advanced Physical Chemistry*, J. H. Wolfenden, London: Oxford, 1938, p. 45). Fit these data to the model and find the optimum values of the parameters.

$T/\text{K}$	15.05	25.20	47.10	67.13	82.11	133.4	204.05	256.5	283.0
$CP/J \text{ K}^{-1} \text{ mol}^{-1}$	0.1943	0.5987	3.5333	7.6360	10.0953	17.8780	22.7202	24.8038	26.0833

Examine the behavior of the fit in the range  $10 \leq T \leq 25$  and comment on this.

[Solution](#)

**2.20.** Suggest a practicable method for determining the enthalpy of formation  $\Delta_f H^\circ$  of gaseous carbon monoxide at 25 °C. (*Note:* Burning graphite in a limited supply of oxygen is not satisfactory, since the product will be a mixture of unburned graphite, CO, and CO<sub>2</sub>.)

[Solution](#)

**2.21.** If the enthalpy of combustion  $\Delta_c H^\circ$  of gaseous cyclopropane, C<sub>3</sub>H<sub>6</sub>, is  $-2091.2 \text{ kJ mol}^{-1}$  at 25 °C, calculate the standard enthalpy of formation  $\Delta_f H^\circ$ .

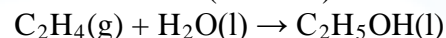
[Solution](#)

**2.22.** The parameters for expressing the temperature dependence of molar heat capacities for various substances listed in Table 2.1 are obtained by fitting the model  $C_{P,m} = d + eT + f/T^2$  to experimental data at various temperatures and finding the values of the parameters  $d$ ,  $e$ , and  $f$  that yield the best fit. Several mathematical software packages (Mathematica, Mathcad, Macsyma, etc.) and several scientific plotting packages (Axum, Origin, PSIPlot, etc.) can perform these fits very quickly. Fit the following data given the temperature dependence of  $C_{P,m}$  for n-butane to the model and obtain the optimum values of the parameters.

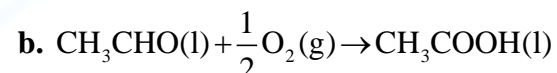
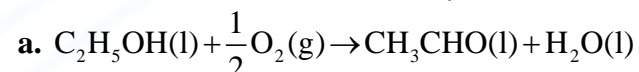
$T/\text{K}$	220	250	275	300	325	350	380	400
$CP/\text{J K}^{-1} \text{mol}^{-1}$	0.642	0.759	0.861	0.952	1.025	1.085	1.142	1.177

[Solution](#)

**2.23.** From the data in Appendix D, calculate  $\Delta H^\circ$  for the reaction (at 25 °C):

[Solution](#)

**2.24.** The bacterium *Acetobacter suboxydans* obtains energy for growth by oxidizing ethanol in two stages, as follows:



The enthalpy increases in the complete combustion (to  $\text{CO}_2$  and liquid  $\text{H}_2\text{O}$ ) of the three compounds are

	$\Delta_c H^\circ/\text{kJ mol}^{-1}$
Ethanol (l)	−1370.7
Acetaldehyde (l)	−1167.3
Acetic acid (l)	−876.1

Calculate the  $\Delta H^\circ$  values for reactions (a) and (b).

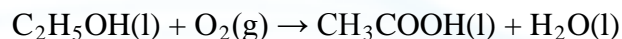
[Solution](#)

**2.25.** The enthalpy of combustion of acrylonitrile ( $\text{C}_3\text{H}_3\text{N}$ ) at 25 °C and 1 atm pressure is  $-1760.9 \text{ kJ mol}^{-1}$  [Stamm, Halverson, and Whalen, *J. Chem. Phys.*, 17, 105(1949)]. Under the same conditions, the heats of formation of  $\text{HCN}(\text{g})$  and  $\text{C}_2\text{H}_2(\text{g})$  from the elements are 135.1 and 226.73  $\text{kJ mol}^{-1}$ , respectively [*The NBS Tables of Chemical and Thermodynamic Properties*, Supp. 2 to Vol. 11 of *J. Phys. Chem. Ref. Data*]. Combining these data with the standard enthalpies of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ , calculate

the enthalpy change in the reaction  $\text{HCN(g)} + \text{C}_2\text{H}_2\text{(g)} \rightarrow \text{H}_2\text{C=CH-CN(g)}$ . [Notes: (a) Assume that the nitrogen present in acrylonitrile is converted into nitrogen gas during combustion. (b) Assume that all substances except for graphite (for the formation of  $\text{CO}_2$ ) are gases, i.e., ignore the fact that acrylonitrile and water will be liquids under the conditions given here.]

[Solution](#)

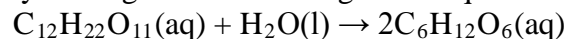
- 2.26.** Calculate  $\Delta H$  for the reaction;



making use of the enthalpies of formation given in Appendix D. Is the result consistent with the results obtained for Problem 2.24?

[Solution](#)

- 2.27.** The disaccharide  $\alpha$ -maltose can be hydrolyzed to glucose according to the equation



Using data in Appendix D and the following values, calculate the standard enthalpy change in this reaction:

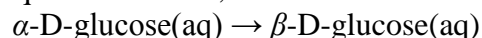
	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{C}_6\text{H}_{12}\text{O}_6\text{(aq)}$	– 1263.1
$\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(aq)}$	– 2238.3

[Solution](#)

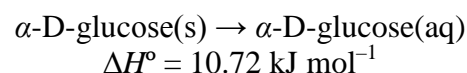
- 2.28.** The standard enthalpy of formation of the fumarate ion is  $-777.4 \text{ kJ mol}^{-1}$ . If the standard enthalpy change of the reaction:
- $$\text{fumarate}^{2-}\text{(aq)} + \text{H}_2\text{(g)} \rightarrow \text{succinate}^{2-}\text{(aq)}$$
- is  $131.4 \text{ kJ mol}^{-1}$ , calculate the enthalpy of formation of the succinate ion.

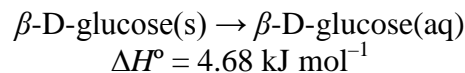
[Solution](#)

- 2.29.** The  $\Delta H^\circ$  for the mutarotation of glucose in aqueous solution,



has been measured in a microcalorimeter and found to be  $-1.16 \text{ kJ mol}^{-1}$ . The enthalpies of solution of the two forms of glucose have been determined to be





Calculate  $\Delta H^\circ$  for the mutarotation of solid  $\alpha\text{-D-glucose}$  to solid  $\beta\text{-D-glucose}$ .

[Solution](#)

- 2.30.** Use the data in Appendix D to calculate  $\Delta H^\circ$  for the hydrolysis of urea into carbon dioxide and ammonia at 25 °C.

[Solution](#)

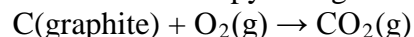
- 2.31.** Here is a problem with a chemical engineering flavor: Ethanol is oxidized to acetic acid in a catalyst chamber at 25 °C. Calculate the rate at which heat will have to be removed (in  $\text{J h}^{-1}$ ) from the chamber in order to maintain the reaction chamber at 25 °C, if the feed rate is 45.00  $\text{kg h}^{-1}$  of ethanol and the conversion rate is 42 mole % of ethanol. Excess oxygen is assumed to be available.

[Solution](#)

- 2.32.** **a.** An ice cube at 0 °C weighing 100.0 g is dropped into 1 kg of water at 20 °C. Does all of the ice melt? If not, how much of it remains? What is the final temperature? The latent heat of fusion of ice at 0 °C is  $6.025 \text{ kJ mol}^{-1}$ , and the molar heat capacity of water,  $C_{P,m}$  is  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ .  
**b.** Perform the same calculations with 10 ice cubes of the same size dropped into the water. (See Problem 3.33 of Chapter 3 for the calculation of the corresponding entropy changes.)

[Solution](#)

- \*2.33.** From the data in Table 2.1 and Appendix D, calculate the enthalpy change in the reaction



at 1000 K.

[Solution](#)

- 2.34.** From the bond strengths in Table 2.2, estimate the enthalpy of formation of gaseous propane,  $\text{C}_3\text{H}_8$ , using the following additional data:

	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{C(graphite)} \rightarrow \text{C(g)}$	716.7
$\text{H}_2(\text{g}) \rightarrow 2\text{H(g)}$	436.0

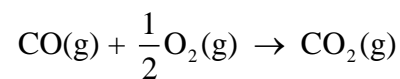
[Solution](#)

- 2.35.** A sample of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  weighing 0.1328 g, was burned to completion in a bomb calorimeter at 25 °C, and the heat evolved was measured to be 2186.0 J.

- Calculate  $\Delta_c U_m$  and  $\Delta_c H_m$  for the combustion of sucrose.
- Use data in Appendix D to calculate  $\Delta_f H_m$  for the formation of sucrose.

[Solution](#)

- 2.36.** The value of  $\Delta H^\circ$  for the reaction



is  $-282.97 \text{ kJ mol}^{-1}$  at 298 K. Calculate  $\Delta U^\circ$  for the reaction.

[Solution](#)

### Ideal Gases

- 2.37.** One mole of an ideal gas initially at 10.00 bar and 298.0 K is allowed to expand against a constant external pressure of 2.000 bar to a final pressure of 2.000 bar. During this process, the temperature of the gas falls to 253.2 K. We wish to construct a reversible path connecting these initial and final steps as a combination of a reversible isothermal expansion followed by a reversible adiabatic expansion. To what volume should we allow the gas to expand isothermally so that subsequent adiabatic expansion is guaranteed to take the gas to the final state? Assume that  $C_{V,m} = \frac{3}{2}R$ .

[Solution](#)

- 2.38.** Two moles of oxygen gas, which can be regarded as ideal with  $C_p = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$  (independent of temperature), are maintained at 273 K in a volume of  $11.35 \text{ dm}^3$ .
- What is the pressure of the gas?
  - What is  $PV$ ?
  - What is  $C_V$ ?

[Solution](#)

**2.39.** Suppose that the gas in Problem 2.38 is heated reversibly to 373 K at constant volume:

- a. How much work is done on the system?
- b. What is the increase in internal energy,  $\Delta U$ ?
- c. How much heat was added to the system?
- d. What is the final pressure?
- e. What is the final value of  $PV$ ?
- f. What is the increase in enthalpy,  $\Delta H$ ?

[Solution](#)

**2.40.** Suppose that the gas in Problem 2.38 is heated reversibly to 373 K at constant pressure.

- a. What is the final volume?
- b. How much work is done on the system?
- c. How much heat is supplied to the system?
- d. What is the increase in enthalpy?
- e. What is the increase in internal energy?

[Solution](#)

**2.41.** Suppose that the gas in Problem 2.38 is reversibly compressed to half its volume at constant temperature (273 K).

- a. What is the change in  $U$ ?
- b. What is the final pressure?
- c. How much work is done on the system?
- d. How much heat flows out of the system?
- e. What is the change in  $H$ ?

[Solution](#)

**2.42.** With the temperature maintained at 0 °C, 2 mol of an ideal gas are allowed to expand against a piston that supports 2 bar pressure. The initial pressure of the gas is 10 bar and the final pressure 2 bar.

- a. How much energy is transferred to the surroundings during the expansion?
- b. What is the change in the internal energy and the enthalpy of the gas?
- c. How much heat has been absorbed by the gas?

[Solution](#)



- 2.43.** Suppose that the gas in Problem 2.42 is allowed to expand *reversibly* and *isothermally* from the initial pressure of 10 bar to the final pressure of 2 bar.
- How much work is done by the gas?
  - What are  $\Delta U$  and  $\Delta H$ ?
  - How much heat is absorbed by the gas?

[Solution](#)

- 2.44.** A sample of hydrogen gas, which may be assumed to be ideal, is initially at 3.0 bar pressure and a temperature of 25.0 °C, and has a volume of 1.5 dm<sup>3</sup>. It is expanded reversibly and adiabatically until the volume is 5.0 dm<sup>3</sup>. The heat capacity  $C_P$  of H<sub>2</sub> is 28.80 J K<sup>-1</sup> mol<sup>-1</sup> and may be assumed to be independent of temperature.
- Calculate the final pressure and temperature after the expansion.
  - Calculate  $\Delta U$  and  $\Delta H$  for the process.

[Solution](#)

- \*2.45.** Initially 0.1 mol of methane is at 1 bar pressure and 80 °C. The gas behaves ideally and the value of  $C_P/C_V$  is 1.31. The gas is allowed to expand reversibly and adiabatically to a pressure of 0.1 bar.
- What are the initial and final volumes of the gas?
  - What is the final temperature?
  - Calculate  $\Delta U$  and  $\Delta H$  for the process.

[Solution](#)

- 2.46.** A gas behaves ideally and its  $C_V$  is given by

$$C_V/\text{J K}^{-1} \text{ mol}^{-1} = 21.52 + 8.2 \times 10^{-3} T/\text{K}$$

- What is  $C_{P,m}$  as a function of  $T$ ?
- A sample of this gas is initially at  $T_1 = 300$  K,  $P_1 = 10$  bar, and  $V_1 = 1$  dm<sup>3</sup>. It is allowed to expand until  $P_2 = 1$  bar and  $V_2 = 10$  dm<sup>3</sup>. What are  $\Delta U$  and  $\Delta H$  for this process? Could the process be carried out adiabatically?

[Solution](#)

- 2.47.** Prove that for an ideal gas two reversible adiabatic curves on a  $P$ - $V$  diagram cannot intersect.

[Solution](#)

- 2.48.** An ideal gas is defined as one that obeys the relationship  $PV = nRT$ . We showed in Section 2.7 that for such gases  $(\partial U/\partial V)_T = 0$  and  $(\partial H/\partial P)_T = 0$

Prove that for an ideal gas  $C_V$  and  $C_P$  are independent of volume and pressure.

[Solution](#)

- 2.49.** One mole of an ideal gas underwent a reversible isothermal expansion until its volume was doubled. If the gas performed 1 kJ of work, what was its temperature?

[Solution](#)

- 2.50.** A gas that behaves ideally was allowed to expand reversibly and adiabatically to twice its volume. Its initial temperature was 25.00 °C, and  $C_{V,m} = (5/2)R$ . Calculate  $\Delta U_m$  and  $\Delta H_m$  for the expansion process.

[Solution](#)

- 2.51.** With  $C_{V,m} = (3/2)R$ , 1 mol of an ideal monatomic gas undergoes a reversible process in which the volume is doubled and in which 1 kJ of heat is absorbed by the gas. The initial pressure is 1 bar and the initial temperature is 300 K. The enthalpy change is 1.50 kJ.
- Calculate the final pressure and temperature.
  - Calculate  $\Delta U$  and  $w$  for the process.

[Solution](#)

- \*2.52.** Prove that

$$C_V = - \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_U$$

[Solution](#)

- \*2.53.** Prove that for an ideal gas the rate of change of the pressure  $dP/dt$  is related to the rates of change of the volume and temperature by

$$\frac{1}{P} \frac{dP}{dt} = - \frac{1}{V} \frac{dV}{dt} + \frac{1}{T} \frac{dT}{dt}$$

[Solution](#)



**\*2.54.** Initially 5 mol of nitrogen are at a temperature of 25 °C and a pressure of 10 bar. The gas may be assumed to be ideal;  $C_{V,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$  and is independent of temperature. Suppose that the pressure is *suddenly* dropped to 1 bar; calculate the final temperature,  $\Delta U$ , and  $\Delta H$ .

[Solution](#)

**2.55.** A chemical reaction occurs at 300 K in a gas mixture that behaves ideally, and the total amount of gas increases by 0.27 mol. If  $\Delta U = 9.4 \text{ kJ}$ , what is  $\Delta H$ ?

[Solution](#)

**2.56.** Suppose that 1.00 mol of an ideal monatomic gas ( $C_V = (3/2)R$ ) at 1 bar is adiabatically and reversibly compressed starting at 25.0 °C from 0.1000 m<sup>3</sup> to 0.0100 m<sup>3</sup>. Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

[Solution](#)

**2.57.** Suppose that an ideal gas undergoes an irreversible isobaric adiabatic process. Derive expressions for  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  and the final temperature of the gas undergoing the process.

[Solution](#)

**2.58.** Exactly one mole of an ideal monatomic gas at 25.0 °C is cooled and allowed to expand from 1.00 dm<sup>3</sup> to 10.00 dm<sup>3</sup> against an external pressure of 1.00 bar. Calculate the final temperature, and  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

[Solution](#)

**2.59.** A balloon 15 m in diameter is inflated with helium at 20 °C.

**a.** What is the mass of helium in the balloon, assuming the gas to be ideal?

**b.** How much work is done by the balloon during the process of inflation against an external pressure of 1 atm (101.315 kPa), from an initial volume of zero to the final volume?

[Solution](#)

- 2.60.** a. Calculate the work done when 1 mol of an ideal gas at 2 bar pressure and 300 K is expanded isothermally to a volume of 1.5 L, with the external pressure held constant at 1.5 bar.  
b. Suppose instead that the gas is expanded isothermally and *reversibly* to the same final volume; calculate the work done.

[Solution](#)

- 2.61.** The heat capacity difference can be determined experimentally in terms of the two variables  $\alpha$  and  $\beta$  in the equation for an ideal gas. Determine the value of  $C_P$  and  $C_V$  for an ideal gas in the equation  $C_P - C_V = TV\alpha^2/\beta$  where

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \text{ and } \beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T .$$

[Solution](#)

### Real Gases

- 2.62.** For an ideal gas,  $PV_m = RT$  and therefore  $(dT/dP)_V = V_m/R$ . Derive the corresponding relationship for a van der Waals gas.

[Solution](#)

- \*2.63.** One mole of a gas at 300 K is compressed isothermally and reversibly from an initial volume of 10 dm<sup>3</sup> to a final volume of 0.2 dm<sup>3</sup>. Calculate the work done on the system if  
a. the gas is ideal.  
b. the equation of state of the gas is  $P(V_m - b) = RT$ , with  $b = 0.03 \text{ dm}^3 \text{ mol}^{-1}$ .  
Explain the difference between the two values.

[Solution](#)

- \*2.64.** One mole of a gas at 100 K is compressed isothermally from an initial volume of 20 dm<sup>3</sup> to a final volume of 5 dm<sup>3</sup>. Calculate the work done on the system if
- the gas is ideal.
  - the equation of state is

$$\left(P + \frac{a}{V_m^2}\right)V_m = RT \text{ where } a = 0.384 \text{ m}^6 \text{ Pa mol}^{-1}$$

[This equation is obeyed approximately at low temperatures, whereas  $P(V_m - b) = RT$  (see Problem 2.63) is obeyed more closely at higher temperatures.] Account for the difference between the values in (a) and (b).

[Solution](#)

- 2.65.** Derive the expression

$$dP = \frac{P dV_m}{V_m - b} - \frac{ab}{V_m^3(V_m - b)} dV_m + \frac{P dT}{T} + \frac{a dT}{V_m^2 T}$$

for 1 mol of a van der Waals gas.

[Solution](#)

- 2.66.** If a substance is burned at constant volume with no heat loss, so that the heat evolved is all used to heat the product gases, the temperature attained is known as the *adiabatic flame temperature*. Calculate this quantity for methane burned at 25 °C in the amount of oxygen required to give complete combustion to CO<sub>2</sub> and H<sub>2</sub>O. Use the data in Appendix D and the following approximate expressions for the heat capacities:

$$\begin{aligned} C_{P,m}(\text{CO}_2)/\text{J K}^{-1} \text{ mol}^{-1} &= 44.22 + 8.79 \times 10^{-3} T/\text{K} \\ C_{P,m}(\text{H}_2\text{O})/\text{J K}^{-1} \text{ mol}^{-1} &= 30.54 + 1.03 \times 10^{-2} T/\text{K} \end{aligned}$$

[Solution](#)

- \*2.67.** Two moles of a gas are compressed isothermally and reversibly, at 300 K, from an initial volume of 10 dm<sup>3</sup> to a final volume of 1 dm<sup>3</sup>. If the equation of state of the gas is  $P(V_m - b) = RT$ , with  $b = 0.04 \text{ dm}^3 \text{ mol}^{-1}$ , calculate the work done on the system,  $\Delta U$ , and  $\Delta H$ .

[Solution](#)

- \*2.68.** Three moles of a gas are compressed isothermally and reversibly, at 300 K, from an initial volume of 20 dm<sup>3</sup> to a final volume of 1 dm<sup>3</sup>. If the equation of state of the gas is

$$\left(P + \frac{n^2 a}{V_m^2}\right) V_m = nRT$$

with  $a = 0.55 \text{ Pa m}^6 \text{ mol}^{-1}$ , calculate the work done,  $\Delta U$ , and  $\Delta H$ .

[Solution](#)

- \*2.69.** One mole of a van der Waals gas at 300 K is compressed isothermally and reversibly from 60 dm<sup>3</sup> to 20 dm<sup>3</sup>. If the constants in the van der Waals equation are

$$a = 0.556 \text{ Pa m}^6 \text{ mol}^{-1} \text{ and } b = 0.064 \text{ dm}^3 \text{ mol}^{-1}$$

calculate  $w_{\text{rev}}$ ,  $\Delta U$ , and  $\Delta H$ .

[Solution](#)

- \*2.70.** Show that the Joule-Thomson coefficient  $\mu$  can be written as:

$$\mu = -\frac{1}{C_p} \left( \frac{\partial H}{\partial P} \right)_T$$

Then, for a van der Waals gas for which  $\mu$  can be written as:

$$\mu = \frac{2a/RT - b}{C_p}$$

calculate  $\Delta H$  for the isothermal compression of 1.00 mol of the gas at 300 K from 1 bar to 100 bar.

[Solution](#)

### Essay Questions

- 2.71.** Explain clearly what is meant by a thermodynamically reversible process. Why is the reversible work done by a system the maximum work?
- 2.72.** Explain the thermodynamic meaning of a system, distinguishing between open, closed, and isolated systems. Which one of these systems is (a) a fish swimming in the sea or (b) an egg?

**Solutions**

**2.1.** A bird weighing 1.5 kg leaves the ground and flies to a height of 75 metres, where it attains a velocity of  $20 \text{ m s}^{-1}$ . What change in energy is involved in the process? (Acceleration of gravity =  $9.81 \text{ m s}^{-2}$ .)

**Solution:**

Given:  $m_{\text{bird}} = 1.5 \text{ kg}$ ,  $h = 75 \text{ m}$ ,  $u = 20 \text{ m s}^{-1}$

Required:  $\Delta E$

Since in this particular system, a bird is starting from rest and moving to a height of 75 meters, there are both potential and kinetic energies that must be considered. First we can find the potential energy which is equivalent to the work required to raise the bird to the given height.

Potential energy;

$$w = mgh$$

$$w = (1.5 \text{ kg})(9.81 \text{ m s}^{-2})(75 \text{ m})$$

$$w = 1\,103.625 \text{ kg m}^2 \text{ s}^{-2}$$

recall that  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and therefore

$$w = 1\,103.6 \text{ J}$$

Kinetic energy;

$$E_k = \frac{1}{2}mu^2$$

$$E_k = \frac{1}{2}(1.5 \text{ kg})(20 \text{ m s}^{-1})^2$$

$$E_k = 300 \text{ kg m}^2 \text{ s}^{-2}$$

just as above,  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and therefore

$$E_k = 300 \text{ J}$$

The energy change of the system can be taken as the sum of both the potential and kinetic energies.

$$\Delta E = E_k + E_p$$

$$\Delta E = (1\,103.6 + 300) \text{ J}$$

$$\Delta E = 1\,403.6 \text{ J}$$

$$\boxed{\Delta E = 1.40 \text{ kJ}}$$

[Back to Problem 2.1](#)

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**2.2.** The densities of ice and water at 0 °C are 0.9168 and 0.9998 g cm<sup>-3</sup>, respectively. If  $\Delta H$  for the fusion process at atmospheric pressure is 6.025 kJ mol<sup>-1</sup>, what is  $\Delta U$ ? How much work is done on the system?

**Solution:**

Given:  $T = 0\text{ }^{\circ}\text{C}$ ,  $\rho_{\text{ice}} = 0.9168\text{ g cm}^{-3}$ ,  $\rho_{\text{water}} = 0.9998\text{ g cm}^{-3}$ ,  $\Delta_{\text{fus}} H = 6.025\text{ kJ mol}^{-1}$

Required:  $\Delta U$ ,  $w$

Since we are given the densities of both ice and water in this system, it is possible to determine the corresponding volumes. Knowing that water and ice are composed of H<sub>2</sub>O we can say that in one mole, the corresponding mass would be approximately 18.0152 g (15.9994 + 2(1.0079)).

one mole of ice has volume;

$$\rho_{\text{ice}} = \frac{m_{\text{ice}}}{V_{\text{ice}}}$$

$$V_{\text{ice}} = \frac{m_{\text{ice}}}{\rho_{\text{ice}}}$$

$$V_{\text{ice}} = \frac{18.0152\text{ g}}{0.9168\text{ g cm}^{-3}}$$

$$V_{\text{ice}} = 19.65\text{ cm}^3$$

One mole of water has volume;

$$\rho_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{V_{\text{H}_2\text{O}}}$$

$$V_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}}$$

$$V_{\text{H}_2\text{O}} = \frac{18.0152\text{ g}}{0.9998\text{ g cm}^{-3}}$$

$$V_{\text{H}_2\text{O}} = 18.02\text{ cm}^3$$

Now find the change in volume due to  $\Delta H$  fusion when moving from ice to water:

$$\Delta V = V_{\text{H}_2\text{O}} - V_{\text{ice}}$$

$$\Delta V = (18.02 - 19.65) \text{ cm}^3$$

$$\Delta V = -1.63 \text{ cm}^3$$

Since we are working with a single mole of ice and water, we can express the volume as

$$\Delta V = -1.63 \text{ cm}^3 \text{ mol}^{-1}$$

We are given the value of the enthalpy of fusion. Enthalpy may be defined by Eq. 2.23;

$$H = U + PV$$

Since the system is under atmospheric pressure, it is possible to determine the amount of PV work done in this process.

Since  $1 \text{ atm dm}^3 = 101.325 \text{ J}$ , we first change the volume into  $\text{dm}^3$ ;

$$\Delta V = -1.63 \cancel{\text{cm}^3} (10^{-3} \text{ dm}^3 \cancel{\text{cm}^{-3}})$$

$$\Delta V = -0.00163 \text{ dm}^3$$

Now the PV work can be found;

$$\Delta PV = (1 \text{ atm})(-0.00163 \text{ dm}^3)$$

$$\Delta PV = -0.00163 \text{ atm dm}^3$$

$$\Delta PV = -0.163 \text{ J}$$

Which can then be expressed as,

$$\Delta PV = -0.163 \text{ J mol}^{-1}$$

$$\boxed{w = \Delta PV = -0.163 \text{ J mol}^{-1}}$$



Now Eq. 2.23 can be rearranged to solve for the internal energy,  $U$ ;

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta U = \Delta H - \Delta(PV)$$

$$\Delta H = 6.025 \text{ kJ mol}^{-1} = 6\,025 \text{ J mol}^{-1}$$

$$\Delta U = 6\,025 \text{ J mol}^{-1} - (-0.163 \text{ J mol}^{-1})$$

Since this is a very small difference and the value of  $\Delta H$  is uncertain in the tenth's unit, we can make the approximation,

$$\Delta H \cong \Delta U$$

$$\boxed{\Delta U = 6.025 \text{ kJ mol}^{-1}}$$

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- 2.3.** The density of liquid water at 100 °C is 0.9584 g cm<sup>-3</sup>, and that of steam at the same temperature is 0.000 596 g cm<sup>-3</sup>. If the enthalpy of evaporation of water at atmospheric pressure is 40.63 kJ mol<sup>-1</sup>, what is  $\Delta U$ ? How much work is done by the system during the evaporation process?

**Solution:**

Given:  $T = 100\text{ °C}$ ,  $\rho_{\text{water}} = 0.9584\text{ g cm}^{-3}$ ,  $\rho_{\text{steam}} = 0.000\ 596\text{ g cm}^{-3}$ ,  $\Delta_{\text{evap}}H = 40.63\text{ kJ mol}^{-1}$

Required:  $\Delta U$ ,  $w$

This problem can be solved in the manner used to solve Problem 2.2. First, calculate the change in volume when moving between states then find the amount of pressure-volume work done on or by the system. Recall that a single mole of H<sub>2</sub>O has an approximate mass of 18.0152 g. The volume of one mole of liquid water at 100 °C is found,

$$\rho_{\text{water}} = \frac{m_{\text{water}}}{V_{\text{water}}}$$

$$V_{\text{water}} = \frac{m_{\text{water}}}{\rho_{\text{water}}}$$

$$V_{\text{ice}} = \frac{18.015\ 2\ \cancel{\text{g}}}{0.958\ 4\ \cancel{\text{g}}\ \text{cm}^{-3}}$$

$$V_{\text{ice}} = 18.797\ 2\ \text{cm}^3$$

The volume of one mole of steam has a volume of,

$$\rho_{\text{steam}} = \frac{m_{\text{steam}}}{V_{\text{steam}}}$$

$$V_{\text{steam}} = \frac{m_{\text{steam}}}{\rho_{\text{steam}}}$$

$$V_{\text{steam}} = \frac{18.015\ 2\ \cancel{\text{g}}}{0.000\ 596\ \cancel{\text{g}}\ \text{cm}^{-3}}$$

$$V_{\text{steam}} = 30\ 226.845\ 6\ \text{cm}^3$$

$$\Delta V = V_{\text{steam}} - V_{\text{water}}$$

$$\Delta V = (30\,226.845\,6 - 18.797\,2) \text{ cm}^3$$

$$\Delta V = 30\,208 \text{ cm}^3$$

Which can then be expressed as,

$$\Delta V = 30.208 \text{ dm}^3 \text{ mol}^{-1}$$

Since  $1 \text{ atm dm}^3 = 101.325 \text{ J}$ , the  $PV$  work can be found;

$$\Delta PV = (1 \text{ atm})(30.208 \text{ dm}^3)$$

$$\Delta PV = 30.208 \text{ atm dm}^3$$

$$\Delta PV = 3\,060.825\,6 \text{ J}$$

Rounding to the proper number of significant figures gives  $3.06 \text{ kJ}$ . Expressed in terms of  $\text{mol}^{-1}$  gives,

$$\Delta PV = 3\,060.825\,6 \text{ J mol}^{-1}$$

$$\boxed{w = \Delta PV = 3.06 \text{ kJ mol}^{-1}}$$

Now Eq. 2.23 can be rearranged to solve for the internal energy,  $U$ ;

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta U = \Delta H - \Delta(PV)$$

Since  $\Delta H = 40.63 \text{ kJ mol}^{-1}$

$$\Delta U = 40.63 \text{ kJ mol}^{-1} - (3.06 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta U = 37.57 \text{ kJ mol}^{-1}}$$

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**2.4.** The latent heat of fusion of water at 0 °C is 6.025 kJ mol<sup>-1</sup> and the molar heat capacities ( $C_{P,m}$ ) of water and ice are 75.3 and 37.7 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. The  $C_P$  values can be taken to be independent of temperature. Calculate  $\Delta H$  for the freezing of 1 mol of supercooled water at -10.0 °C.

**Solution:**

Given:  $T = 0\text{ °C}$ ,  $q_{\text{fus}} = 6.025\text{ kJ mol}^{-1}$ ,  $C_{P,\text{water}} = 75.3\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $C_{P,\text{ice}} = 37.7\text{ J K}^{-1}\text{ mol}^{-1}$

Required:  $\Delta_{\text{freeze}} H$

Because the latent heat of fusion of water is given at 0 °C and we start with supercooled water at -10.0 °C. We will first heat up the supercooled water to 0 °C, go through a state change from water to ice, and then cool down the ice from 0 °C to -10.0 °C.

The amount of heat that needs to be supplied to increase the temperature of 1 mole of substance from  $T_{\text{lower}}$  to  $T_{\text{higher}}$  at constant pressure is given by,

$$q_{P,m} = \int_{T_{\text{lower}}}^{T_{\text{higher}}} C_{P,m} dT$$

If  $C_{P,m}$  is independent of temperature, then the integral will reduce to;

$$q_{P,m} = C_{P,m} (T_{\text{higher}} - T_{\text{lower}}) = \Delta H_m$$

Therefore, when heating water from -10°C to 0°C, we will get:

$$q_1 = C_P (T_{\text{higher}} - T_{\text{lower}})$$

$$q_1 = 75.3\text{ J K}^{-1}\text{ mol}^{-1} (273.15 - 263.15)\text{ K}$$

$$q_1 = 753\text{ J mol}^{-1}$$

The latent heat of fusion of water is given at 0 °C. Therefore, the latent heat for the change of state from water to ice is:

$$q_2 = -6\,025\text{ J mol}^{-1}$$

Cooling the ice from 0 °C to -10 °C we obtain,

$$q_3 = C_p (T_2 - T_1)$$

$$q_3 = -37.7 \text{ J } \cancel{\text{K}} \text{ mol}^{-1} (273.15 - 263.15) \cancel{\text{K}}$$

$$q_3 = -377 \text{ J mol}^{-1}$$

Now finding the net heat;

$$q_{\text{net}} = q_1 + q_2 + q_3$$

$$q_{\text{net}} = (753 - 6\,025 - 377) \text{ J mol}^{-1}$$

$$q_{\text{net}} = -5\,649 \text{ J mol}^{-1}$$

$$q_{\text{net}} = \Delta_{\text{freeze}} H$$

$$\boxed{\Delta_{\text{freeze}} H = -5.65 \text{ kJ mol}^{-1}}$$

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**2.5.** A sample of liquid acetone weighing 0.700 g was burned in a bomb calorimeter for which the heat capacity (including the sample) is  $6937 \text{ J K}^{-1}$ . The observed temperature rise was from  $25.00^\circ\text{C}$  to  $26.69^\circ\text{C}$ .

**a.** Calculate  $\Delta U$  for the combustion of 1 mol of acetone.

**b.** Calculate  $\Delta H$  for the combustion of 1 mol of acetone.

**Solution:**

Given:  $m_{\text{acetone}} = 0.700 \text{ g}$ ,  $C_{V,m} = 6937 \text{ J K}^{-1}$ ,  $T = 25.00^\circ\text{C}$ ,  $T_f = 26.69^\circ\text{C}$

Required:  $\Delta U$  and  $\Delta H$

Acetone has a molar mass of  $M_{\text{acetone}} = 58.08 \text{ g mol}^{-1}$  therefore it is possible to determine the number of moles of acetone present as well as the amount of heat evolved per mole of acetone burned. It is important to note that bomb calorimeters work under conditions of *constant volume* and therefore Eq. 2.28 applies:

The heat required to raise the temperature of 1 mole of material from  $T_1$  to  $T_2$  at constant volume is given by;

$$q_{V,m} = \int_{T_1}^{T_2} C_{V,m} dT$$

$$q_{V,m} = C_{V,m} (T_2 - T_1)$$

$$q_{V,m} = (6937 \text{ J K}^{-1})(299.84 - 298.15) \text{ K}$$

$$q_{V,m} = 11\,723.53 \text{ J}$$

$$q_{V,m} = 11.72 \text{ kJ}$$

Again, using the fact that the bomb calorimeter operates at constant volume, it can be simply stated that;

$$\Delta U = -q_{V,m}$$

$$\Delta U = -11.72 \text{ kJ}$$

The heat evolved during the combustion of a single mole is given by;

$$\Delta U_m = -q_{V,m} \times \frac{M}{m}$$

$$\Delta U_m = (-11\,723.53\text{ J}) \times \frac{58.08\text{ g mol}^{-1}}{0.700\text{ g}}$$

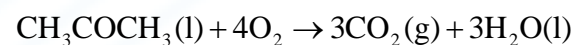
$$\Delta U_m = -972\,718\text{ J mol}^{-1}$$

$$\boxed{\Delta U_m = -972.72\text{ kJ mol}^{-1}}$$

Assuming that the Ideal Gas Law applies,

$$\Delta(PV) = \Delta nRT$$

Since the balanced reaction may be written as follows;



The change in moles for the gaseous species is;

$$\Delta n = n_{\text{products}} - n_{\text{reactants}}$$

$$\Delta n = 3 - 4$$

$$\Delta n = -1$$

Now the enthalpy can be found using the assumption above:

$$\Delta(PV) = (-1) \left( 8.3145\text{ J K}^{-1}\text{ mol}^{-1} \right) (299.84\text{ K})$$

$$\Delta(PV) = -2\,493.02\text{ J mol}^{-1}$$

Recall that we can now solve for the enthalpy from Eq. 2.41,

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = -972\,718\text{ J mol}^{-1} + (-2493.02\text{ J mol}^{-1})$$

$$\Delta H = -975\,211\text{ J mol}^{-1}$$

$$\boxed{\Delta H = -975.21\text{ kJ mol}^{-1}}$$

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**2.6.** An average man weighs about 70 kg and produces about 10 460 kJ of heat per day.

**a.** Suppose that a man were an isolated system and that his heat capacity were

$4.18 \text{ J K}^{-1} \text{ g}^{-1}$ ; if his temperature were  $37^\circ\text{C}$  at a given time, what would be his temperature 24 h later?

**b.** A man is in fact an open system, and the main mechanism for maintaining his temperature constant is evaporation of water. If the enthalpy of vaporization of water at  $37^\circ\text{C}$  is  $43.4 \text{ kJ mol}^{-1}$ , how much water needs to be evaporated per day to keep the temperature constant?

**Solution:**

Given:  $m_{\text{man}} = 70 \text{ kg}$ , heat =  $q = 10\,460 \text{ kJ}$ ,  $C_p = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$ ,  $T = 37^\circ\text{C}$ ,  $\Delta_{\text{vap}}H = 43.4 \text{ kJ mol}^{-1}$

Required:  $T$  at 24 hrs,  $m_{\text{water}}$

**a.** First, we start by putting the heat capacity in terms of  $\text{J K}^{-1}$  by using the man's mass.

$$C_p = (4.18 \text{ J K}^{-1} \text{ g}^{-1})(70\,000 \text{ g})$$

$$C_p = 292\,600 \text{ J K}^{-1}$$

The rise in temperature can then be found using the specific heat (heat capacity) as well as the amount of heat produced by the man per day.

$$\Delta T = \frac{q}{C_p}$$

$$\Delta T = \frac{10\,460\,000 \text{ J}}{292\,600 \text{ J K}^{-1}}$$

$$\Delta T = 35.75 \text{ K}$$

And using the initial temperature, the temperature at 24 hours can be found,

$$\Delta T = T_{24\text{hrs}} - T_0$$

$$T_{24\text{hrs}} = \Delta T + T_0$$

$$T_{24\text{hrs}} = 35.75 \text{ K} + 310.15 \text{ K}$$

$$T_{24\text{hrs}} = 345.9 \text{ K}$$

$$\boxed{T_{24\text{hrs}} = 72.8^\circ\text{C}}$$

- b.** We can use the enthalpy of vaporization of water as well as its molar mass (18.0152 g mol<sup>-1</sup>) in order to determine the amount of water required to keep the man's temperature constant;

$$\Delta H = \frac{43\,400 \text{ J mol}^{-1}}{18.0152 \text{ g mol}^{-1}}$$

$$\Delta H = 2\,409.08 \text{ J g}^{-1}$$

$$m_{\text{water}} = \frac{q}{\Delta H}$$

$$m_{\text{water}} = \frac{10\,460\,000 \cancel{\text{J}}}{2\,409.08 \cancel{\text{J}} \text{ g}^{-1}}$$

$$m_{\text{water}} = 4\,341.9 \text{ g}$$

$$\boxed{m_{\text{water}} = 4.34 \text{ kg}}$$

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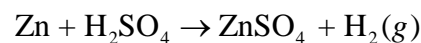
**2.7.** In an open beaker at 25 °C and 1 atm pressure, 100 g of zinc are caused to react with dilute sulfuric acid. Calculate the work done by the liberated hydrogen gas, assuming it behaves ideally. What would be the work done if the reaction took place in a sealed vessel?

**Solution:**

Given:  $T = 25\text{ °C}$ ,  $P = 1\text{ atm}$ ,  $m_{\text{Zn}} = 100\text{ g}$

Required:  $w_{\text{H}_2}$

The balanced equation for this reaction is given by;



We can see that for each mole of zinc reacted, one mole of hydrogen gas is produced. One hundred grams of zinc (molar mass 65.39 g mol<sup>-1</sup>) will then produce;

$$n_{\text{Zn}} = \frac{m}{M}$$

$$n_{\text{Zn}} = \frac{100\cancel{\text{ g}}}{65.39\cancel{\text{ g}}\text{ mol}^{-1}}$$

$$n_{\text{Zn}} = 1.529\text{ mol}$$

and since  $n_{\text{Zn}} = n_{\text{H}_2}$

$$n_{\text{H}_2} = 1.529\text{ mol}$$

The work *done by* the *open system* is *PV* work and can be expressed as;

$$-w = \Delta(PV) = n_{\text{H}_2}RT$$

Remember that when the system **DOES** work, you need to include the negative sign!

$$-w = (1.529 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 + 25) \text{ K}$$

$$-w = 3\,791 \text{ J}$$

$$w = -3.79 \text{ kJ}$$

In a *sealed vessel*, the conditions would be such that there was no change in volume meaning that there would be no work done.

In a closed vessel;

$$w = 0 \text{ kJ}$$

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- 2.8.** A balloon is 0.50 m in diameter and contains air at 25 °C and 1 bar pressure. It is then filled with air isothermally and reversibly until the pressure reaches 5 bar. Assume that the pressure is proportional to the diameter of the balloon and calculate (a) the final diameter of the balloon and (b) the work done in the process.

**Solution:**

Given:  $d_{\text{balloon}} = 0.50 \text{ m}$ ,  $T = 25 \text{ °C}$ ,  $P_1 = 1 \text{ bar}$ ,  $P_2 = 5 \text{ bar}$

Required:  $d_{\text{balloon}}$  final,  $w_{\text{balloon}}$

- a) If we make the assumption that the pressure is proportional to the diameter of the balloon and  $D_i$  and  $D_f$  are the diameters in the initial and final case, then we can write;

$$P_1 = kD_1$$

Where  $k$  is then expressed as;

$$k = \frac{P_1}{D_1}$$

$$k = \frac{1 \text{ bar}}{0.50 \text{ m}}$$

$$k = 2 \text{ bar m}^{-1}$$

At the final pressure,  $P_2$  we can see that:

$$P_2 = kD_2$$

$$D_2 = \frac{P_2}{k}$$

$$D_2 = \frac{5 \text{ bar}}{2 \text{ bar m}^{-1}}$$

$$D_2 = 2.5 \text{ m}$$

The final diameter of the balloon is

$$d_{\text{balloon}} = 2.5 \text{ m}$$

b) The work done in the process of filling the balloon with air isothermally and reversibly is defined by Eq. 2.11;

$$w_{\text{rev}} = -\int_{V_1}^{V_2} P dV$$

Using geometry, we can show the relationship between volume and diameter in order to solve the above equation.

The balloon will be treated as a sphere:

$$V_{\text{sphere}} = \frac{4}{3} \pi r^3$$

Remember that the radius is defined as half of the diameter, thus;

$$V_{\text{sphere}} = \frac{4}{3} \pi \left( \frac{D}{2} \right)^3$$

Now we can differentiate both sides to get:

$$dV_{\text{sphere}} = \frac{4}{3} \cdot \frac{3}{8} \pi D^2 dD$$

$$dV_{\text{sphere}} = \frac{1}{2} \pi D^2 dD$$

Now we can make this substitution into Eq. 2.11 in order to solve for the work done.

$$-w_{\text{rev}} = \int_{V_1}^{V_2} P dV$$

And because of the volume proportionality to the diameter,

$$-w_{\text{rev}} = \int_{D_1}^{D_2} P dV$$

Let us now use  $P = kD$  and substitute

$$-w_{\text{rev}} = \int_{D_1}^{D_2} kD dV$$

$$-w_{\text{rev}} = \int_{D_1}^{D_2} kD \frac{1}{2} \pi D^2 dD$$

Which can be simplified to:

$$-w_{\text{rev}} = \frac{1}{2} \pi k \int_{D_1}^{D_2} D^3 dD$$

This expression can now be solved by integrating from  $D_1$  to  $D_2$ ,

$$-w_{\text{rev}} = \frac{1}{2} \left( \frac{1}{4} \right) \pi k (D_2^4 - D_1^4)$$

$$-w_{\text{rev}} = \left( \frac{1}{8} \right) \pi (2.5^4 - 0.5^4) \{ \text{bar m}^{-1} \text{ m}^4 \}$$

$$-w_{\text{rev}} = 30.6 \text{ bar m}^3$$

Since  $1 \text{ bar} = 10^5 \text{ Pa}$ ,  $1 \text{ Pa} = \text{kg m}^{-1} \text{ s}^{-2}$  and  $1 \text{ J} = \text{kg m}^2 \text{ s}^{-2}$  then we get;

$$-w_{\text{rev}} = (30.6 \cancel{\text{ bar}} \text{ m}^3) (10^5 \text{ Pa } \cancel{\text{ bar}^{-1}})$$

$$-w_{\text{rev}} = 3\,063\,052 \text{ Pa m}^3$$

$$-w_{\text{rev}} = 3\,063\,052 \text{ kg m}^{-1} \text{ s}^{-2} \text{ m}^3$$

$$-w_{\text{rev}} = 3\,063\,052 \text{ kg m}^2 \text{ s}^{-2}$$

$$-w_{\text{rev}} = 3\,063\,052 \text{ J}$$

$$\boxed{w_{\text{balloon}} = -3\,063 \text{ kJ}}$$

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**2.9.** When 1 cal of heat is given to 1 g of water at 14.5 °C, the temperature rises to 15.5 °C. Calculate the molar heat capacity of water at 15 °C.

**Solution:**

Given:  $q = 1$  cal,  $m_{\text{water}} = 1$  g,  $T_1 = 14.5$  °C,  $T_2 = 15.5$  °C

Required:  $C_p$  at 15 °C

Using the mass and known molar mass for water ( $18.0152$  g mol<sup>-1</sup>), we can find the number of moles that will absorb 1 cal of heat;

$$n_{\text{water}} = \frac{m}{M}$$

$$n_{\text{water}} = \frac{1.00 \cancel{\text{g}}}{18.0152 \cancel{\text{g}} \text{ mol}^{-1}}$$

$$n_{\text{water}} = 0.0555 \text{ mol}$$

Since 1 cal = 4.184 J we can then find the heat capacity according to Eq. 2.25 or Eq. 2.27 depending on the conditions;

$$C_v = \frac{dq_v}{dT} \quad (\text{Eq. 2.25})$$

$$C_p = \frac{dq_p}{dT} = \left( \frac{\partial H}{\partial T} \right)_p \quad (\text{Eq. 2.27})$$

More generally, because we have not been given the system's conditions;

$$C = \frac{q}{\Delta T}$$

$$C = \frac{1 \text{ cal}}{[(15.5 + 273.15) - (14.5 + 273.15)] \text{ K}} \text{ or } C = \frac{4.184 \text{ J}}{1 \text{ K}}$$

$$C = 4.184 \text{ J K}^{-1}$$

The molar heat capacity would then be;



$$C_m = \frac{q}{n\Delta T} = \frac{C}{n}$$

$$C_m = \frac{4.184 \text{ J K}^{-1}}{0.0555 \text{ mol}} = 75.387 \text{ 387 39 J K}^{-1} \text{ mol}^{-1} \rightarrow \boxed{C_m = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**2.10.** A vessel containing 1.000 kg of water at 25.00 °C is heated until it boils. How much heat is supplied? How long would it take a one-kilowatt heater to supply this amount of heat? Assume the heat capacity calculated in Problem 2.9 to apply over the temperature range.

**Solution:**

Given:  $m_{\text{water}} = 1.000 \text{ kg}$ ,  $T = 25.00 \text{ °C}$ ,  $C_m = 75.387 \text{ J K}^{-1} \text{ mol}^{-1}$  (calculated in problem 2.9)

Required:  $q$ ,  $t_{\text{heater operation}}$

Recall that the boiling point for water is 100 °C so this will be our final temperature which will yield a change in temperature of 75.0 °C (or 75 K). In order to determine the amount of heat required to heat the water from one temperature to the next, we must first find the number of moles of water heated. The molar mass for water is  $18.0152 \text{ g mol}^{-1}$ .

$$n_{\text{water}} = \frac{m}{M}$$

$$n_{\text{water}} = \frac{1000 \cancel{\text{ g}}}{18.0152 \cancel{\text{ g}} \text{ mol}^{-1}}$$

$$n_{\text{water}} = 55.5087 \text{ mol}$$

Remember that:

$$C_m = \frac{q}{n\Delta T}$$

So we can rearrange this and solve for the heat:

$$q = C_m n \Delta T$$

$$q = (75.387 \text{ J } \cancel{\text{ K}^{-1}} \cancel{\text{ mol}^{-1}}) (55.5087 \cancel{\text{ mol}}) (75.0 \cancel{\text{ K}})$$

$$q = 313\,849 \text{ J}$$

$$\boxed{q = 314 \text{ kJ}}$$

A 1 kW heater can supply the heat in 314 seconds since  $1 \text{ kW} = 1000 \text{ W}$  and one  $1 \text{ J} = 1 \text{ W s}$  and  $1 \text{ kJ} = 1 \text{ kW s}$ ;

$$t_{\text{heater}} = 314 \text{ s}$$

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**2.11.** A nonporous ceramic of volume  $V \text{ m}^3$  and mass  $M \text{ kg}$  is immersed in a liquid of density  $d \text{ kg m}^{-3}$ . What is the work done on the ceramic if it is slowly raised a height  $h \text{ m}$  through the liquid? Neglect any resistance caused by viscosity. What is the change in the potential energy of the ceramic?

**Solution:**

Given:  $V = \text{m}^3$ ,  $M = \text{kg}$ ,  $d = \text{kg m}^{-3}$

Required:  $w$ ,  $\Delta E_p$

Since we can neglect any resistance caused by the viscosity of the liquid, we can say that the apparent mass of the ceramic decreases by the mass of liquid that is displaced when it is raised.

The mass of the liquid can be defined as;

$$M_l = Vd \text{ kg}$$

While the apparent mass of the ceramic can be defined as;

$$M_c = M - M_l$$

$$M_c = (M - Vd) \text{ kg}$$

The work done when raising a mass is given by;

$$w = mgh$$

Where  $g$  is the earth's gravitational constant and making the correct substitutions;

$$w = (M - Vd) gh \text{ kg m s}^{-2} \text{ m}$$

$$w = (M - Vd) gh \text{ kg m}^2 \text{ s}^{-2}$$

Since  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ , we write,

$$\boxed{w = (M - Vd) gh \text{ J}}$$

When moving a mass from rest to a certain height, the work done on the mass also represents the potential energy change.

$$\Delta E_p = (M - Vd) gh \text{ J}$$

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**2.12.** Show that the differential  $dP$  of the pressure of an ideal gas is an exact differential.

**Solution:**

We have already learned that variables such as internal energy and volume ( $U$  and  $V$ ) are state functions. This means that these functions are independent of the path taken.

Since the path of the integral for the differential is not important; meaning, you can take *any path* to get to the same result, the differential is called **exact**. Variables such as  $q$  and  $w$  have differentials which are *path dependent*; and are thus **inexact**. Integrating over these paths is more difficult since the integrals do not reduce to a simple difference of two boundary values. They represent areas over which we must integrate.

Euler's Criterion for Exactness states that if;

$$dz = M(x, y)dx + N(x, y)dy \quad (\text{Eq. 2.17})$$

where  $M$  and  $N$  are functions of the independent variables  $x$  and  $y$ . We must then take the mixed partials of  $M$  and  $N$  and determine whether they are equal to one another or not.

If:

$$M(x, y) = \left( \frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N(x, y) = \left( \frac{\partial z}{\partial y} \right)_x$$

we need to show that the mixed partial derivatives are equivalent:

$$\left[ \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right]_x = \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y$$

Thus we can say that:

$$\left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial N}{\partial x} \right)_y$$

This relationship must be satisfied if  $dz$  is an exact differential (i.e. it meets Euler Criterion for Exactness). These equations can be found in the textbook, Eq.2.17 to Eq.2.22.

From the Ideal Gas Law we know that  $PV = nRT$ . From Appendix C, the total derivative of  $P$  is a function of both  $T$  and  $V$ . Thus, for a single mole of gas:  $P = \frac{RT}{V}$ .

Differentiating both sides, we get:

$$dP = -\frac{RT}{V^2}dV + \frac{R}{V}dT$$

Applying Euler's theorem gives

$$\text{LHS: } \frac{\partial}{\partial T} \left( -\frac{RT}{V^2} \right) = -\frac{R}{V^2}$$

$$\text{RHS: } \frac{\partial}{\partial V} \left( \frac{R}{V} \right) = -\frac{R}{V^2}$$

LHS = RHS and therefore, the differential is *exact* and  $P$  is a *state function*.

$$\left[ \frac{\partial}{\partial T} \left( -\frac{RT}{V^2} \right) = \frac{\partial}{\partial V} \left( \frac{R}{V} \right) \right]$$

$$\boxed{dP = \text{exact}}$$

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**2.13.** Determine whether  $dU = xy^2dx + x^2ydy$  is an exact differential. If it is find the function  $U$  of which  $dU$  is the differential. Do this by integrating over suitable paths. In a plot of  $y$  against  $x$ , show a plot of the paths that you chose.

**Solution:**

Given:  $dU = xy^2dx + x^2ydy$

Required: exact or inexact? plot  $y$  vs  $x$ .

In order to test for the exactness of the differential  $dU$ , we will again use the Euler test for exactness described in problem 2.14.

Differentiating both sides we can then say that  $dz$  is equal to  $dU$  and,

$$dU = xy^2dx + x^2ydy$$

$$M(x, y) = \left( \frac{\partial U}{\partial x} \right)_y \quad \text{and} \quad N(x, y) = \left( \frac{\partial U}{\partial y} \right)_x$$

Now taking the mixed partial derivatives yields;

$$\left( \frac{\partial M}{\partial y} \right)_x = 2xy \quad \text{and} \quad \left( \frac{\partial N}{\partial x} \right)_y = 2xy$$

$$\boxed{\left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial N}{\partial x} \right)_y}$$

$$\boxed{dU = \text{exact}}$$

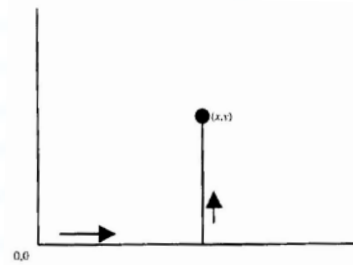
$dU$ , because it is exact, it also describes a state function.

Since the mixed partials are equivalent, we know that taking the integral of  $dU$  will result in a simple difference between the beginning and end points (ie. the path to a single result is not important). The integral can be given by;

$$\int^{x,y} dU = \int_A xy^2dx + \int_B x^2ydy$$

Let A and B be two segments which lead to the final position  $(x,y)$ . We can use a path which simplifies the integration by choosing the origin  $(0,0)$  to  $x$  on the A segment. Here,  $y=0$  so this integral will equal zero. In the second segment, segment B,  $x$  has a specific value and  $y$  varies from  $(0,0)$  to  $y$ .





The integral reduces to:

$$\int dU = x^2 \int_0^y y dy$$

$$\int dU = \frac{1}{2} x^2 y^2 + C$$

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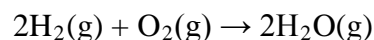
**2.14.** Using the data given in Table 2.1 and Appendix D, find the enthalpy change for the reaction  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$  at 800 K.

**Solution:**

Given: Table 2.1 and Appendix D

Required:  $\Delta H_m(T_2)$

From Table 2.1 we are given the following information regarding the reaction



All of the values given in Appendix D correspond to the standard states: 25.00 °C and 1 bar pressure.

$\text{H}_2\text{O}(\text{g})$ :

$$\Delta_f H^\circ = -241.826 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ = -237.2 \text{ kJ mol}^{-1}$$

$$S^\circ = 188.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At a temperature of 800 K and using equations 2.50 through 2.52 we obtain;

$$\Delta H_m(T_2) - \Delta H_m(T_1) = \int_{T_1}^{T_2} \Delta C_p dT \quad (\text{Eq. 2.50})$$

If  $\Delta H_m(T_1)$  is known for  $T_1 = 25.00^\circ\text{C}$ , the  $\Delta$  value of  $H_m(T_2)$  at any temperature  $T_2$  can be found.

$$\Delta H_m(T_2) = \Delta H_m(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

Now we can make a substitution for  $\Delta C_p$  using Eq. 2.49 ;

$$\Delta H_m(T_2) = \Delta H_m(T_1) + \int_{T_1}^{T_2} (\Delta d + \Delta eT + \Delta fT^{-2}) dT \quad (\text{Eq. 2.51})$$

$$\Delta H_m(T_2) = \Delta H_m(T_1) + \Delta d(T_2 - T_1) + \frac{1}{2}\Delta e(T_2^2 - T_1^2) - \Delta f\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (\text{Eq. 2.52})$$

From the values in Table 2.1 we obtain,

$$\Delta d = d_{\text{products}} - d_{\text{reactants}}$$

$$\Delta d = 2d_{\text{H}_2\text{O}} - (2d_{\text{H}_2} + d_{\text{O}_2})$$

$$\Delta d = (2 \times 30.54 \text{ J K}^{-1} \text{ mol}^{-1}) - (2 \times 27.28 + 29.96) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta d = (61.08 - 84.52) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta d = -23.44 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta e = e_{\text{products}} - e_{\text{reactants}}$$

$$\Delta e = 2e_{\text{H}_2\text{O}} - (2e_{\text{H}_2} + e_{\text{O}_2})$$

$$\Delta e = (2 \times 10.29 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}) - (2 \times 3.26 \times 10^{-3} + 4.18 \times 10^{-3}) \text{ J K}^{-2} \text{ mol}^{-1}$$

$$\Delta e = (0.02058 - 0.0107) \text{ J K}^{-2} \text{ mol}^{-1}$$

$$\Delta e = 9.88 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$\Delta f = f_{\text{products}} - f_{\text{reactants}}$$

$$\Delta f = 2f_{\text{H}_2\text{O}} - (2f_{\text{H}_2} + f_{\text{O}_2})$$

$$\Delta f = (2 \times 0) - (2 \times 5.0 \times 10^4 - 1.67 \times 10^5) \text{ J K mol}^{-1}$$

$$\Delta f = 67\,000 \text{ J K mol}^{-1}$$

$$\Delta f = 6.7 \times 10^4 \text{ J K mol}^{-1}$$

First we need to calculate the enthalpy for this reaction at 298.15 K (for 2 moles);

$$\Delta H^\circ(298.15 \text{ K}) = 2\Delta_f H^\circ = 2(-241.826 \text{ kJ mol}^{-1})$$

$$\Delta H^\circ(298.15 \text{ K}) = -483.652 \text{ kJ mol}^{-1}$$

And making all substitutions into Eq. 2.52 we obtain,

$$\begin{aligned}\Delta H_m(800\text{ K}) &= -483\,652\text{ J mol}^{-1} + \left(-23.44\text{ J K}^{-1}\text{ mol}^{-1}\right)(800-298.15)\text{ K} \\ &+ \frac{1}{2}\left(9.88 \times 10^{-3}\text{ J K}^{-2}\text{ mol}^{-1}\right)(800^2 - 298.15^2)\text{ K}^2 \\ &- \left(6.7 \times 10^4\text{ J K mol}^{-1}\right)\left(\frac{1}{800} - \frac{1}{298.15}\right)\text{ K}^{-1}\end{aligned}$$

$$\Delta H_m(800\text{ K}) = (-483\,652 - 11\,763.364 + 2\,722.466\,493 + 141.969\,101\,1)\text{ J mol}^{-1}$$

$$\Delta H_m(800\text{ K}) = -492\,550.928\,4$$

$$\boxed{\Delta H_m(800\text{ K}) = -492.55\text{ kJ mol}^{-1}}$$

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**2.15.** A sample of liquid benzene weighing 0.633 g is burned in a bomb calorimeter at 25.00 °C, and 26.54 kJ of heat are evolved.

**a.** Calculate  $\Delta U_m$

**b.** Calculate  $\Delta H_m$

**Solution:**

Given:  $m_{\text{benzene}} = 0.633 \text{ g}$ ,  $T = 25 \text{ °C}$ ,  $q = 26.54 \text{ kJ}$

Required:  $\Delta U_m$  and  $\Delta H_m$

- a.** First, it is important to remember that when using a bomb calorimeter, we are working with a constant volume. Also, the water surrounding the bomb increases in temperature but gradually loses heat to the surroundings. Second, since benzene has the molecular formula  $\text{C}_6\text{H}_6$ , it has a molar mass of approximately  $78.1121 \text{ g mol}^{-1}$ . With this latter information, the number of moles of benzene can be found.

$$n_{\text{benzene}} = \frac{m}{M}$$

$$n_{\text{benzene}} = \frac{0.633 \cancel{\text{ g}}}{78.1121 \cancel{\text{ g}} \text{ mol}^{-1}}$$

$$n_{\text{benzene}} = 0.008104 \text{ mol}$$

The heat evolved in the combustion of 1 mole of benzene is given by,

$$q_m = \frac{26.54 \text{ kJ}}{0.008104 \text{ mol}}$$

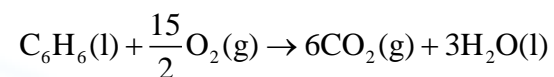
$$q_m = 3275 \text{ kJ mol}^{-1}$$

Recall that when working with a bomb calorimeter as described earlier, the internal energy is

$\Delta U_m = -q_m$  and therefore,

$$\boxed{\Delta U_m = -3275 \text{ kJ mol}^{-1}}$$

- b.** The balanced equation for this reaction is:



We have already seen Eq. 2.41,  $\Delta H = \Delta U + \Delta(PV)$  many times. However, in this case, we can work under the assumption that  $\Delta(PV) = \Delta n(RT)$  which gives;

$$\Delta H_m = \Delta U_m + \Delta n(RT)$$

$$\text{where } \Delta n = 6 - \frac{15}{2} = -1.5$$

Making the appropriate substitutions;

$$\Delta H_m = -3\,274\,900 \text{ kJ mol}^{-1} + (-1.5)(8.3145 \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1})(298.15 \text{ } \cancel{\text{K}})$$

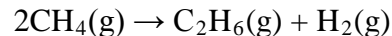
$$\Delta H_m = -3\,278\,618.452 \text{ J mol}^{-1}$$

$$\boxed{\Delta H_m = -3\,279 \text{ kJ mol}^{-1}}$$

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**2.16.** Deduce the standard enthalpy change for the process:



(data in Appendix D)

**Solution:**

Given: Appendix D

Required:  $\Delta H^\circ$

All information given in the tables of Appendix D correspond to the standard states  $T = 25.00^\circ\text{C}$  and 1 bar pressure. Enthalpies of formation allow us to calculate enthalpies of any reaction provided that we know the  $\Delta_f H^\circ$  values for all reactants and all products. The standard enthalpy change may be found using Eq. 2.53:

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

Using the information provided in Appendix D for the reaction:



$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = \Delta H^\circ(\text{C}_2\text{H}_6, \text{g}) + \Delta H^\circ(\text{H}_2, \text{g}) - 2[\Delta H^\circ(\text{CH}_4, \text{g})]$$

$$\Delta H^\circ = [-84.0 + 0 - (2)(-74.6)] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = 65.2 \text{ kJ mol}^{-1}}$$

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- 2.17.** A sample of liquid methanol weighing 5.27 g was burned in a bomb calorimeter at 25.00 °C, and 119.50 kJ of heat was evolved (after correction for standard conditions).
- Calculate  $\Delta_c H^\circ$  for the combustion of 1 mol of methanol.
  - Use this value and the data in Appendix D for  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$  to obtain a value for  $\Delta_f H^\circ(\text{CH}_3\text{OH}, \text{l})$ , and compare with the value given in the table.
  - If the enthalpy of vaporization of methanol is  $35.27 \text{ kJ mol}^{-1}$ , calculate  $\Delta_f H^\circ$  for  $\text{CH}_3\text{OH}(\text{g})$ .

**Solution:**

Given:  $m_{\text{methanol}} = 5.27 \text{ g}$ ,  $T = 25^\circ\text{C}$ ,  $q = 119.50 \text{ kJ}$

Required:  $\Delta_c H^\circ$ ,  $\Delta_f H^\circ(\text{CH}_3\text{OH}, \text{l})$ ,  $\Delta_f H^\circ(\text{CH}_3\text{OH}, \text{g})$

- a.** Remember that when we are working with bomb calorimeters, the conditions are such that volume remains constant. Knowing that methanol has the molecular formula  $\text{CH}_3\text{OH}$ , we can determine the molar mass: approximately  $32.04 \text{ g mol}^{-1}$ . With this, we can determine the number of moles burned in the reaction.

$$n_{\text{methanol}} = \frac{m}{M}$$

$$n_{\text{methanol}} = \frac{5.27 \cancel{\text{g}}}{32.04 \cancel{\text{g}} \text{ mol}^{-1}}$$

$$n_{\text{methanol}} = 0.164\,481\,897 \text{ mol}$$

Using the heat evolved during the reaction, it is possible to determine the change in internal energy if you remember that:  $\Delta U = -q$  at constant volume.



$$q_{V,m} = \frac{q}{n_{\text{methanol}}}$$

$$q_{V,m} = \frac{119.50 \text{ kJ}}{0.164\,481\,897 \text{ mol}}$$

$$q_{V,m} = 726.523\,7192 \text{ kJ mol}^{-1}$$

$$\Delta_c U^0 = -q_{V,m}$$

$$\Delta_c U^0 = -726\,523.7192 \text{ J mol}^{-1}$$

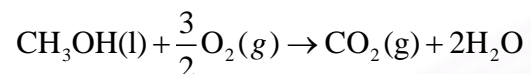
In this case, we can work under the assumption that  $\Delta(PV) = \Delta nRT$  so we can use the following equation to solve for the enthalpy of combustion:

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta_c H^0 = \Delta_c U^0 + \Delta n(RT)$$

$$\Delta_c H^0 = -726\,523.7192 \text{ J mol}^{-1} + \Delta n(RT)$$

The balanced reaction is written as;



$$\Delta n(\text{for gaseous species}) = 1 - \frac{3}{2}$$

$$\Delta n = -0.5$$

And by making the appropriate substitutions we obtain,

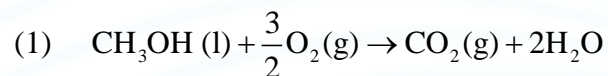
$$\Delta_c H^0 = -726\,523.7192 \text{ J mol}^{-1} + \Delta n(RT)$$

$$\Delta_c H^0 = -726\,523.7192 \text{ J mol}^{-1} + (-0.5)(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})$$

$$\Delta_c H^0 = -727\,763.2033 \text{ J mol}^{-1}$$

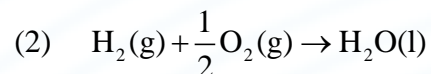
$$\boxed{\Delta_c H^0 = -727.8 \text{ kJ mol}^{-1}}$$

b. The balanced reaction is as follows,

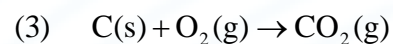


where  $\Delta_c H^\circ = -727.8 \text{ kJ mol}^{-1}$

Using data from Appendix D, for  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , we have the following reactions:

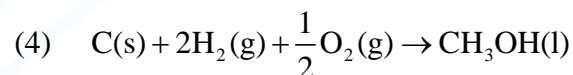


where  $\Delta_f H^\circ = -285.830 \text{ kJ mol}^{-1}$



where  $\Delta_f H^\circ = -393.51 \text{ kJ mol}^{-1}$

Both of these reactions can be coupled in order to produce methanol:



This is done by multiplying the second equation (2) by 2 and adding it to the third equation (3) and subtracting equation one (1).

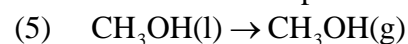
$$\Delta_f H^\circ = 2\Delta_f H^\circ(\text{H}_2\text{O}) + \Delta_f H^\circ(\text{CO}_2) - \Delta_f H^\circ(2\text{H}_2\text{O})$$

$$\Delta_f H^\circ = [(2 \times -285.830) - 393.51 + 727.8] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_f H^\circ = -237.4 \text{ kJ mol}^{-1}}$$

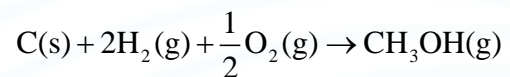
c. The value given in Appendix D is  $\Delta_f H^\circ = -239.2 \text{ kJ mol}^{-1}$ , which differs only very slightly from the value found through the coupling of the three equations. They might have used different data which would account for the disparity.

The reaction for the vaporization of methanol is as follows:



Where we are given that  $\Delta_v H^\circ = 32.27 \text{ kJ mol}^{-1}$

We can now couple equations 4 and 5 in order to get



$$\Delta_f H^\circ(\text{CH}_3\text{OH, g}) = \Delta_f H^\circ(\text{Eq.4}) + \Delta_v H^\circ(\text{Eq.5})$$

$$\Delta_f H^\circ(\text{CH}_3\text{OH, g}) = (-237.5 + 35.27) \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_f H^\circ(\text{CH}_3\text{OH, g}) = -202.2 \text{ kJ mol}^{-1}}$$

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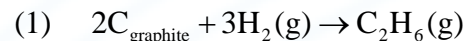
**2.18.** Calculate the heat of combustion ( $\Delta_c H^\circ$ ) of ethane from the data given in Appendix D.

**Solution:**

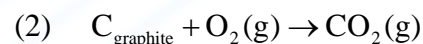
Given: Appendix D

Required:  $\Delta_c H^\circ$

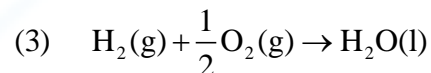
All of the values given in Appendix D were taken under the standard conditions of  $T=25.00^\circ\text{C}$  and 1 bar pressure. The reaction for the combustion of ethane can be found by coupling equations 1 through 3 in the following manner (all enthalpies from Appendix D):



where  $\Delta_f H^\circ = -84.0 \text{ kJ mol}^{-1}$

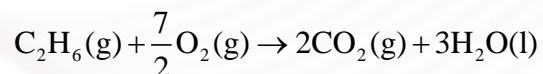


where  $\Delta_f H^\circ = -393.51 \text{ kJ mol}^{-1}$



where  $\Delta_f H^\circ = -285.830 \text{ kJ mol}^{-1}$

In order to get the reaction for the combustion of ethane, we need to multiply Eq. 3 by 3, add it to Eq. 2 multiplied by 2 then subtract Eq. 1 from the mix. This series of operations yields;



$$\Delta_c H^\circ = 3\Delta_f H^\circ(\text{Eq. 3}) + 2\Delta_f H^\circ(\text{Eq. 2}) - \Delta_f H^\circ(\text{Eq. 1})$$

$$\Delta_c H^\circ = \left[ (3 \times -285.830) + (2 \times -393.51) - (-84.0) \right] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_c H^\circ = -1560.5 \text{ kJ mol}^{-1}}$$

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**2.19.** The model used to describe the temperature dependence of heat capacities (Eq. 2.48; Table 2.1) cannot remain valid as the temperature approaches absolute zero because of the  $1/T^2$  term. In some cases, the model starts to break down at temperatures significantly higher than absolute zero. The following data for nickel are taken from a very old textbook (*Numerical Problems in Advanced Physical Chemistry*, J. H. Wolfenden, London: Oxford, 1938, p. 45). Fit these data to the model and find the optimum values of the parameters.

$T/\text{K}$	15.05	25.20	47.10	67.13	82.11	133.4	204.05	256.5	283.0
$CP/\text{J K}^{-1} \text{ mol}^{-1}$	0.1943	0.5987	3.5333	7.6360	10.0953	17.8780	22.7202	24.8038	26.0833

Examine the behavior of the fit in the range  $10 \leq T \leq 25$  and comment on this.

**Solution:**

First we need to perform a multiple regression on the equation  $z = d + ex + fy$  using the following definitions:

$$z = C_{p,m}$$

$$x = T$$

$$y = \frac{1}{T^2}$$

Once we have finished making all the appropriate substitutions, we will obtain the following expression;

$$z = 1.7267 + 9.3424 \times 10^{-2} x - 871.4 y$$

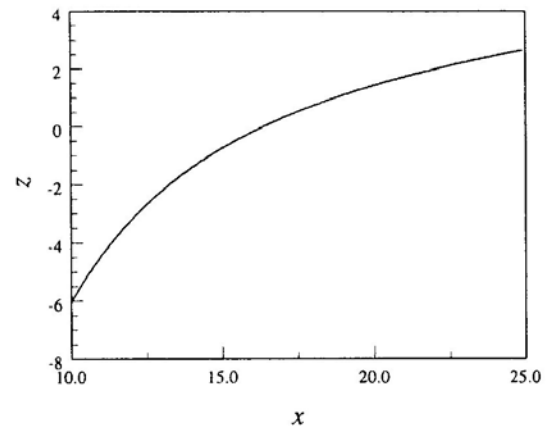
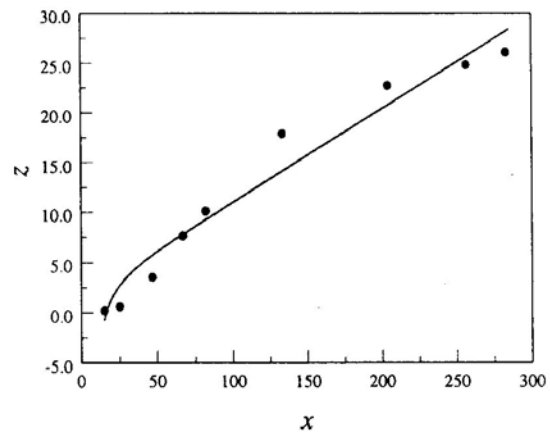
In other words, we find that,

$$d = 1.7267 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$e = 9.3424 \times 10^{-2} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$f = -871.4 \times 10^2 \text{ J K mol}^{-1}$$

Below, we have presented two plots of this function. One is in the range of  $15 \leq T \leq 275$  and the other is in the range of  $10 \leq T \leq 25$ . It can be seen that the function becomes negative at  $T \leq 16.1 \text{ K}$ . It is important to realize that a negative heat capacity is not physically possible. This is therefore an indication that the temperature dependence of heat capacities of solids at low temperature cannot be expressed using the model that we have implemented here. Check out Chapter 16 Section 5 for more information on this subject.

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**2.20.** Suggest a practicable method for determining the enthalpy of formation  $\Delta_f H^\circ$  of gaseous carbon monoxide at 25 °C. (*Note:* Burning graphite in a limited supply of oxygen is not satisfactory, since the product will be a mixture of unburned graphite, CO, and CO<sub>2</sub>.)

**Solution:**

In order to determine the enthalpy of formation for gaseous carbon monoxide, we can measure the heat of combustion of graphite, gaseous carbon monoxide and gaseous carbon dioxide. With this information it will then be possible to determine the enthalpy of formation by using Hess' Law which states that:

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

This can be rewritten using the enthalpies of combustion and solving for the enthalpy of formation for carbon monoxide.

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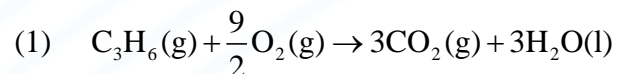
**2.21.** If the enthalpy of combustion  $\Delta_c H^\circ$  of gaseous cyclopropane,  $\text{C}_3\text{H}_6$ , is  $-2091.2 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ , calculate the standard enthalpy of formation  $\Delta_f H^\circ$ .

**Solution:**

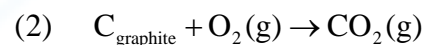
Given:  $\Delta_c H^\circ = -2091.2 \text{ kJ mol}^{-1}$ ,  $T = 25^\circ\text{C}$

Required:  $\Delta_f H^\circ(\text{cyclopropane})$

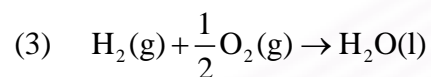
This problem can be solved in the same manner as was done in problem 2.18. However, this time we will be working in reverse as we are given the enthalpy of combustion and we must find the enthalpy of formation. We will start with the reaction for the combustion of cyclopropane.



We are given the enthalpy of combustion in the problem, so now we need to consider the reaction for the formation of both  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$

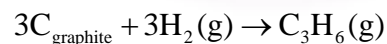


Which has  $\Delta_f H^\circ = -393.51 \text{ kJ mol}^{-1}$  according to Appendix D



Which has  $\Delta_f H^\circ = -285.830 \text{ kJ mol}^{-1}$  according to Appendix D

In order to formulate the correct balanced reaction for the formation of cyclopropane, we must multiply Eq. 2 by 3, add it to Eq. 3 multiplied by 3 and then subtract Eq. 1 from the result.



We must now perform the same operations on the enthalpies of formation and combustion for each reaction, which yields:



$$\Delta_f H^\circ(\text{cyclopropane}) = 3\Delta_f H^\circ(\text{CO}_2) + 3\Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_c H^\circ(\text{cyclopropane})$$

$$\Delta_f H^\circ(\text{cyclopropane}) = 53.2 \text{ kJ mol}^{-1}$$

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**2.22.** The parameters for expressing the temperature dependence of molar heat capacities for various substances listed in Table 2.1 are obtained by fitting the model  $C_{P,m} = d + eT + f/T^2$  to experimental data at various temperatures and finding the values of the parameters  $d$ ,  $e$ , and  $f$  that yield the best fit. Several mathematical software packages (Mathematica, Mathcad, Macsyma, etc.) and several scientific plotting packages (Axum, Origin, PSIPlot, etc.) can perform these fits very quickly. Fit the following data given the temperature dependence of  $C_{P,m}$  for n-butane to the model and obtain the optimum values of the parameters.

$T/\text{K}$	220	250	275	300	325	350	380	400
$CP/\text{J K}^{-1} \text{ mol}^{-1}$	0.642	0.759	0.861	0.952	1.025	1.085	1.142	1.177

**Solution:**

Just as we have already done in problem 2.19 we must perform a multiple regression on the following expression:

$$z = d + ex + fy$$

Using the same definitions as before, we have,

$$z = C_{P,m}$$

$$x = T$$

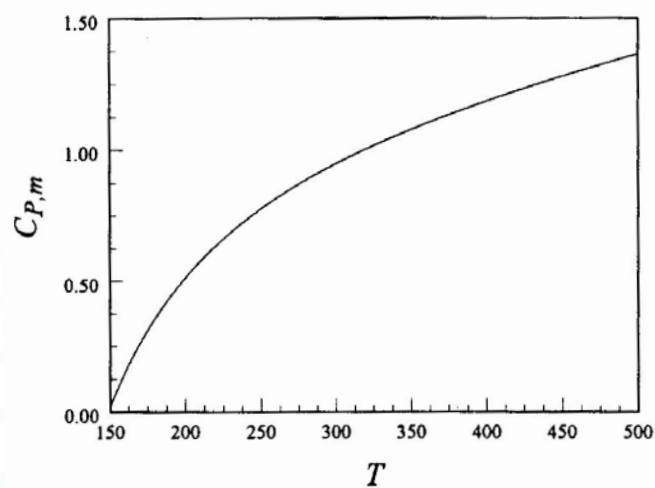
$$y = \frac{1}{T^2}$$

$$z = 0.80053 + 1.303 \times 10^{-3}x - 21991.0y$$

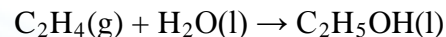
$$d = 0.801 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$e = 1.303 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$f = -2.199 \times 10^4 \text{ J K mol}^{-1}$$

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**2.23.** From the data in Appendix D, calculate  $\Delta H^\circ$  for the reaction (at 25 °C):



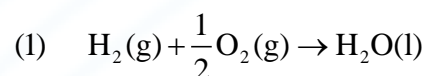
**Solution:**

Given: Appendix D

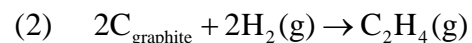
Required:  $\Delta H^\circ$

This problem can be solved in the same way as Problem 2.21. It is always important to outline all of the reactions that can be used to build the final reaction given above. We will need the reactions and enthalpies for the formation of  $\text{H}_2\text{O}(\text{l})$  and  $\text{C}_2\text{H}_4(\text{g})$ . Since we are already given the reaction for the formation of ethanol, all we need to do is take its enthalpy of formation from Appendix D.

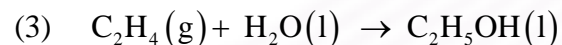
Remember that all values reported in Appendix D were taken under the standard conditions of  $T = 25.00^\circ\text{C}$  and 1 bar pressure.



Which has  $\Delta_f H^\circ = -285.830 \text{ kJ mol}^{-1}$  according to Appendix D



Which has  $\Delta_f H^\circ = 52.4 \text{ kJ mol}^{-1}$  according to Appendix D



Which has  $\Delta_f H^\circ = -277.6 \text{ kJ mol}^{-1}$  according to Appendix D

Since we need the reverse of reactions for Eqs. 1 and 2, we can simply reverse the signs of  $\Delta H^\circ$  to get;

$$\Delta H^\circ = -\Delta_f H^\circ(\text{H}_2\text{O}) + (-\Delta_f H^\circ(\text{C}_2\text{H}_4) + \Delta_f H^\circ(\text{C}_2\text{H}_5\text{OH}))$$

Rather than using this simply logic, we may use Eq. 2.53 which states that:

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = \Delta_f H^\circ(\text{C}_2\text{H}_5\text{OH}) - [\Delta_f H^\circ(\text{H}_2\text{O}) + \Delta_f H^\circ(\text{C}_2\text{H}_4)]$$

Both procedures give the same value:

$$\Delta H^\circ = -277.6 - (-285.830 + 52.4) \text{ kJ mol}^{-1}$$

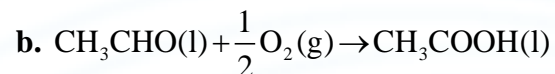
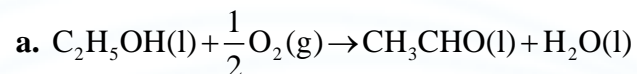
$$\Delta H^\circ = [-277.6 + 285.830 - 52.4] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -44.2 \text{ kJ mol}^{-1}}$$

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**2.24.** The bacterium *Acetobacter suboxydans* obtains energy for growth by oxidizing ethanol in two stages, as follows:



The enthalpy increases in the complete combustion (to  $\text{CO}_2$  and liquid  $\text{H}_2\text{O}$ ) of the three compounds are

	$\Delta_c H^\circ / \text{kJ mol}^{-1}$
Ethanol (l)	-1370.7
Acetaldehyde (l)	-1167.3
Acetic acid (l)	-876.1

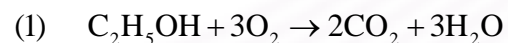
Calculate the  $\Delta H^\circ$  values for reactions (a) and (b).

**Solution:**

Given: See statement of problem

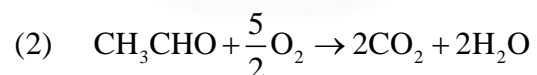
Required:  $\Delta H^\circ$

- a. This problem can be solved in the same way as problem 2.23. It is always important to outline all of the reactions that can be used to build the final two reactions given above. The pertinent reactions are as follows:



This is for the combustion of ethanol and we are given the enthalpy of combustion.

$$\Delta_c H^\circ = -1370.7 \text{ kJ mol}^{-1}$$



This is for the combustion of acetaldehyde and we are given the enthalpy of combustion.

$$\Delta_c H^\circ = -1167.3 \text{ kJ mol}^{-1}$$



This is for the combustion of acetic acid and we are given the enthalpy of combustion.

$$\Delta_c H^\circ = -876.1 \text{ kJ mol}^{-1}$$

Using Eq. 2.53, we can determine the enthalpies for reactions A and B:

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$$

Reaction A:

$$\Delta H^\circ = \Delta_f H^\circ(\text{CH}_3\text{CHO}) - \Delta_f H^\circ(\text{C}_2\text{H}_5\text{OH})$$

Remember that we are given the COMBUSTION enthalpies, so the enthalpies of FORMATION will be equal in magnitude but opposite in sign. This is very important!

$$\Delta H^\circ = -\Delta_c H^\circ(\text{CH}_3\text{CHO}) - (-\Delta_c H^\circ(\text{C}_2\text{H}_5\text{OH}))$$

$$\Delta H^\circ = (-1370.7 + 1167.3) \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -203.4 \text{ kJ mol}^{-1}}$$

**b.** Reaction B:

$$\Delta H^\circ = \Delta_f H^\circ(\text{CH}_3\text{COOH}) - \Delta_f H^\circ(\text{CH}_3\text{CHO})$$

Using the same logic behind whether we are given the enthalpies of combustion or formation and based on the direction of the reactions, we determine that:

$$\Delta H^\circ = -\Delta_c H^\circ(\text{CH}_3\text{COOH}) + (\Delta_c H^\circ(\text{CH}_3\text{CHO}))$$

$$\Delta H^\circ = [ -(-876.1) + (-1167.3) ] \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = (876.1 - 1167.3) \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -291.2 \text{ kJ mol}^{-1}}$$

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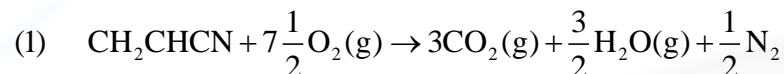
**2.25.** The enthalpy of combustion of acrylonitrile ( $\text{C}_3\text{H}_3\text{N}$ ) at  $25^\circ\text{C}$  and 1 atm pressure is  $-1760.9\text{ kJ mol}^{-1}$  [Stamm, Halverson, and Whalen, *J. Chem. Phys.*, 17, 105(1949)]. Under the same conditions, the heats of formation of  $\text{HCN}(\text{g})$  and  $\text{C}_2\text{H}_2(\text{g})$  from the elements are  $135.1$  and  $226.73\text{ kJ mol}^{-1}$ , respectively [*The NBS Tables of Chemical and Thermodynamic Properties*, Supp. 2 to Vol. 11 of *J. Phys. Chem. Ref. Data*]. Combining these data with the standard enthalpies of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ , calculate the enthalpy change in the reaction  $\text{HCN}(\text{g}) + \text{C}_2\text{H}_2(\text{g}) \rightarrow \text{H}_2\text{C}=\text{CH}-\text{CN}(\text{g})$ . [Notes: (a) Assume that the nitrogen present in acrylonitrile is converted into nitrogen gas during combustion. (b) Assume that all substances except for graphite (for the formation of  $\text{CO}_2$ ) are gases, i.e., ignore the fact that acrylonitrile and water will be liquids under the conditions given here.]

**Solution:**

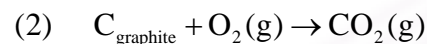
Given: see above

Required:  $\Delta H^\circ$

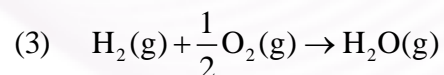
We will be using the same principles for many of these problems so it is always important to compile a list of all relevant reactions so that they can be easily manipulated and used for reference when trying to see where a particular reaction came from (ie. coupling to form new products). Here is a list of all of the reactions involved:



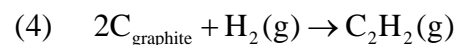
we are given that  $\Delta_c H^\circ = -1760.9\text{ kJ mol}^{-1}$



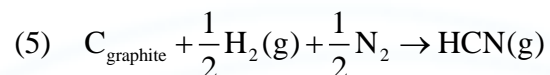
from Appendix D, we know that  $\Delta_f H^\circ = -393.51\text{ kJ mol}^{-1}$



from Appendix D, we know that  $\Delta_f H^\circ = -241.83\text{ kJ mol}^{-1}$



we are given that  $\Delta_f H^\circ = 226.73\text{ kJ mol}^{-1}$



we are given that  $\Delta_f H^\circ = 135.10 \text{ kJ mol}^{-1}$

In order to generate the desired reaction;  $\text{HCN}(\text{g}) + \text{C}_2\text{H}_2(\text{g}) \rightarrow \text{H}_2\text{C}=\text{CH}-\text{CN}(\text{g})$  the following manipulations need to be made to the above five equations.

$$3(\text{Eq.2}) + \frac{3}{2}(\text{Eq.3}) - (\text{Eq.1}) - (\text{Eq.4}) - (\text{Eq.5})$$

Remember that we need to perform these manipulations on the enthalpies as well which yields;

$$3(\text{Eq.2}) + \frac{3}{2}(\text{Eq.3}) - (\text{Eq.1}) - (\text{Eq.4}) - (\text{Eq.5})$$

$$\Delta H^\circ = 3\Delta_f H^\circ(\text{CO}_2) + \frac{3}{2}\Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_c H^\circ(\text{CH}_2\text{CHCN}) - \Delta_f H^\circ(\text{C}_2\text{H}_2) - \Delta_f H^\circ(\text{HCN})$$

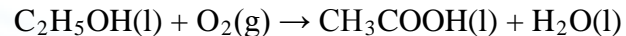
$$\Delta H^\circ = \left[ (3 \times -393.51) + \left( \frac{3}{2} \times -241.83 \right) - (-1\,760.9) - 226.73 - 135.10 \right] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -144.2 \text{ kJ mol}^{-1}}$$

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**2.26.** Calculate  $\Delta H$  for the reaction;



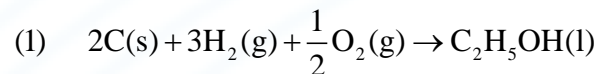
making use of the enthalpies of formation given in Appendix D. Is the result consistent with the results obtained for Problem 2.24?

**Solution:**

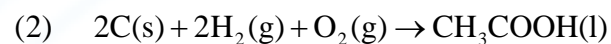
Given: Appendix D

Required:  $\Delta H$  for the reaction

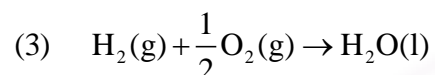
We will begin by defining the reactions that involve the formation of methanol, acetic acid and water. Recall that all values given in Appendix D were taken at the standard temperature of 25.00 °C and 1 bar pressure. From Appendix D, we have;



$$\Delta_f H^\circ = -277.6 \text{ kJ mol}^{-1}$$

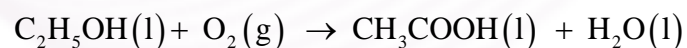


$$\Delta_f H^\circ = -484.3 \text{ kJ mol}^{-1}$$

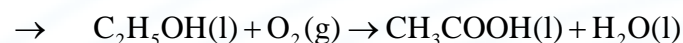
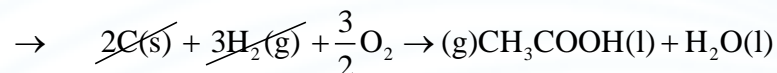
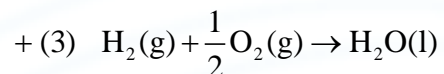
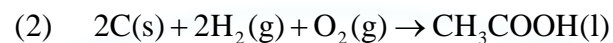


$$\Delta_f H^\circ = -285.830 \text{ kJ mol}^{-1}$$

In order to formulate the wanted reaction;



We must add Eq. 3 to Eq. 2 then subtract Eq. 1 from the sum which yields;



Making the same manipulations on the enthalpies, we obtain,

$$\Delta H^\circ = \Delta_f H^\circ(\text{Eq.2}) + \Delta_f H^\circ(\text{Eq.3}) - \Delta_f H^\circ(\text{Eq.1})$$

$$\Delta H^\circ = [(-484.3) + (-285.83) - (-277.6)] \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = (-484.3 - 285.83 + 277.6) \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -492.53 \text{ kJ mol}^{-1}}$$

Recall that from problem 2.24 we come to the conclusion that:

Reaction A:

$$\Delta H^\circ = \Delta_f H^\circ(\text{CH}_3\text{CHO}) - \Delta_f H^\circ(\text{C}_2\text{H}_5\text{OH})$$

$$\boxed{\Delta H^\circ = -203.4 \text{ kJ mol}^{-1}}$$

Reaction B:

$$\Delta H^\circ = \Delta_f H^\circ(\text{CH}_3\text{COOH}) - \Delta_f H^\circ(\text{CH}_3\text{CHO})$$

$$\boxed{\Delta H^\circ = -291.2 \text{ kJ mol}^{-1}}$$

This will produce a slightly different answer than the one we have obtained.

$$\Delta H^\circ = \Delta H^\circ(\text{reaction A}) + \Delta H^\circ(\text{reaction B})$$

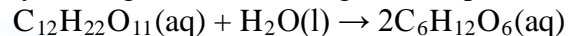
$$\Delta H^\circ = [-203.4 + (-291.2)] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -494.6 \text{ kJ mol}^{-1}}$$

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**2.27.** The disaccharide  $\alpha$ -maltose can be hydrolyzed to glucose according to the equation



Using data in Appendix D and the following values, calculate the standard enthalpy change in this reaction:

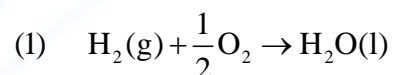
	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$	$-1263.1$
$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq})$	$-2238.3$

**Solution:**

Given: Appendix D

Required:  $\Delta H^\circ$

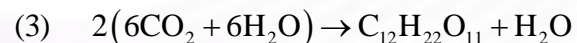
This problem will be solved in the same way that we have solved all similar problems. Let us first make a list of the important reactions involved in the process. From Appendix D we have:



$$\Delta_f H^\circ = -285.83 \text{ kJ mol}^{-1}$$



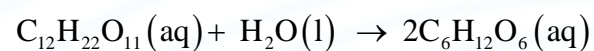
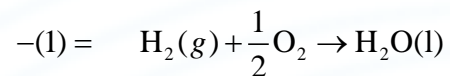
We are given that  $\Delta_f H^\circ = -1263.1 \text{ kJ mol}^{-1}$



We are given that  $\Delta_f H^\circ = -2238.3 \text{ kJ mol}^{-1}$

In order to create the wanted reaction:  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$

We must multiply Eq. 2 by two then subtract Eq. 3 and Eq. 1 which yields:



This must then be done for the enthalpies of formation which gives,

$$\Delta H^\circ = 2\Delta H^\circ(\text{Eq.2}) - \Delta H^\circ(\text{Eq.3}) - \Delta H^\circ(\text{Eq.1})$$

$$\Delta H^\circ = [(2 \times -1263.1) - (-2238.3) - (-285.83)] \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -2.07 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -2.1 \text{ kJ mol}^{-1}}$$

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**2.28.** The standard enthalpy of formation of the fumarate ion is  $-777.4 \text{ kJ mol}^{-1}$ . If the standard enthalpy change of the reaction:  
$$\text{fumarate}^{2-}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{succinate}^{2-}(\text{aq})$$
is  $131.4 \text{ kJ mol}^{-1}$ , calculate the enthalpy of formation of the succinate ion.

**Solution:**

Given:  $\Delta_f H^\circ(\text{fumarate}) = -777.4 \text{ kJ mol}^{-1}$ ,  $\Delta H^\circ = 131.4 \text{ kJ mol}^{-1}$

Required:  $\Delta_f H^\circ(\text{succinate})$

Now we are given the standard enthalpy change for a reaction and we are asked to calculate the enthalpy of formation for the succinate ion. We can do this by rearranging what we already know and solving for the unknown. This is based on the same method that we have been practicing for many of the problems throughout this chapter.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = \Delta_f H^\circ(\text{succinate}) - \Delta_f H^\circ(\text{fumarate})$$

Given that:

$$\Delta_f H^\circ(\text{fumarate}) = -777.4 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(\text{rxn}) = 131.4 \text{ kJ mol}^{-1}$$

Then we can say that:

$$\Delta H^\circ = \Delta_f H^\circ(\text{succinate}) - \Delta_f H^\circ(\text{fumarate})$$

$$131.4 \text{ kJ mol}^{-1} = \Delta_f H^\circ(\text{succinate}) - (-777.4 \text{ kJ mol}^{-1})$$

$$131.4 \text{ kJ mol}^{-1} = \Delta_f H^\circ(\text{succinate}) + 777.4 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{succinate}) = (131.4 - 777.4) \text{ kJ mol}^{-1}$$

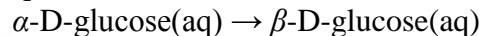
$$\boxed{\Delta_f H^\circ(\text{succinate}) = -646.0 \text{ kJ mol}^{-1}}$$

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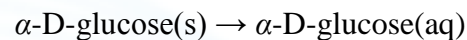
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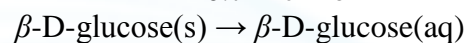
**2.29.** The  $\Delta H^\circ$  for the mutarotation of glucose in aqueous solution,



has been measured in a microcalorimeter and found to be  $-1.16 \text{ kJ mol}^{-1}$ . The enthalpies of solution of the two forms of glucose have been determined to be



$$\Delta H^\circ = 10.72 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ = 4.68 \text{ kJ mol}^{-1}$$

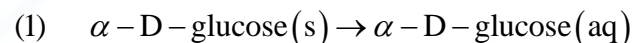
Calculate  $\Delta H^\circ$  for the mutarotation of solid  $\alpha$ -D-glucose to solid  $\beta$ -D-glucose.

**Solution:**

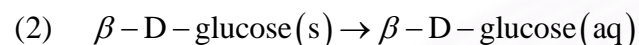
Given:  $\Delta H^\circ = -1.16 \text{ kJ mol}^{-1}$ ,  $\Delta H^\circ_\alpha = 10.72 \text{ kJ mol}^{-1}$ ,  $\Delta H^\circ_\beta = 4.68 \text{ kJ mol}^{-1}$

Required:  $\Delta H^\circ$ (mutarotation) in solid state

We are given that;

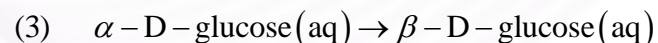


$$\Delta H^\circ = 10.72 \text{ kJ mol}^{-1}$$



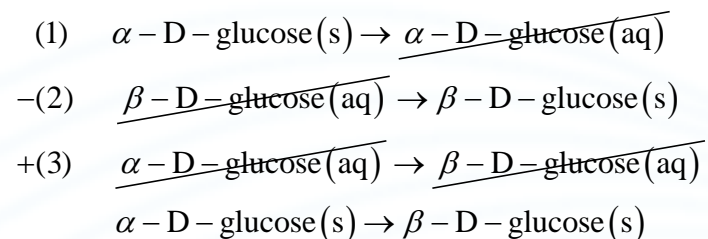
$$\Delta H^\circ = 4.68 \text{ kJ mol}^{-1}$$

And for the mutarotation in the aqueous state we have;



$$\Delta H^\circ = -1.16 \text{ kJ mol}^{-1}$$

Therefore we obtain  $\alpha\text{-D-glucose(s)} \rightarrow \beta\text{-D-glucose(s)}$  by adding Eqs. 1, 2 and 3.



Now we can perform the same operations on the enthalpies of solution in order to obtain,

$$\Delta H^\circ = \Delta_s H^\circ(\text{Eq.1}) - \Delta_s H^\circ(\text{Eq.2}) + \Delta_s H^\circ(\text{Eq.3})$$

It is important to note that we use the reversed sign on Eq. 2 because we need to use the reverse reaction. Always keep this in mind when doing problems like this; otherwise it can become confusing!

$$\Delta H^\circ = \Delta_s H^\circ(\text{Eq.1}) - \Delta_s H^\circ(\text{Eq.2}) + \Delta_s H^\circ(\text{Eq.3})$$

$$\Delta H^\circ = (10.72 - 4.68 - 1.16) \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ(\text{mutarotation}) = 4.88 \text{ kJ mol}^{-1}}$$

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**2.30.** Use the data in Appendix D to calculate  $\Delta H^\circ$  for the hydrolysis of urea into carbon dioxide and ammonia at 25 °C.

**Solution:**

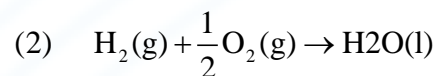
Given: Appendix D,  $T = 25\text{ °C}$

Required:  $\Delta H^\circ$

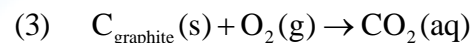
Remember that all values given in Appendix D were taken at the standard temperature and pressure of 25.00 °C and 1 bar pressure. The reaction for the hydrolysis of urea is as follows:



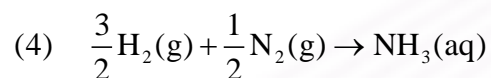
Let us now list the reactions needed in order to generate Eq.1.



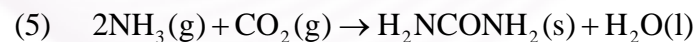
$\Delta_f H^\circ = -285.830\text{ kJ mol}^{-1}$  from Appendix D



$\Delta_f H^\circ = -413.26\text{ kJ mol}^{-1}$  from Appendix D

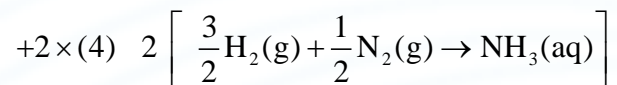
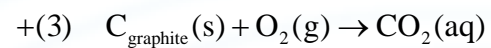
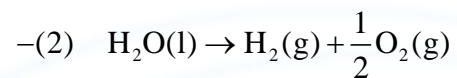


$\Delta_f H^\circ = -80.29\text{ kJ mol}^{-1}$  from Appendix D



$\Delta_f H^\circ = -333.1\text{ kJ mol}^{-1}$

In order to obtain reaction (1), we need to multiply both Eqs. 2 and 5 by -1 then add them to Eq. 3 and Eq. 4 multiplied by 2.



Making the same operations on the enthalpies of formation we obtain,

$$\Delta H^\circ = -\Delta_f H^\circ(\text{Eq.2}) + \Delta_f H^\circ(\text{Eq.3}) + 2\Delta_f H^\circ(\text{Eq.4}) - \Delta_f H^\circ(\text{Eq.5})$$

$$\Delta H^\circ = [ -(-285.83) + (-413.26) + (2 \times -80.29) - (-333.1) ] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = 45.09 \text{ kJ mol}^{-1}}$$

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**2.31.** Here is a problem with a chemical engineering flavor: Ethanol is oxidized to acetic acid in a catalyst chamber at 25 °C. Calculate the rate at which heat will have to be removed (in J h<sup>-1</sup>) from the chamber in order to maintain the reaction chamber at 25 °C, if the feed rate is 45.00 kg h<sup>-1</sup> of ethanol and the conversion rate is 42 mole % of ethanol. Excess oxygen is assumed to be available.

**Solution:**

Given:  $T = 25\text{ °C}$ ,  $v_{\text{feed}} = 45.00\text{ kg h}^{-1}$ ,  $v_{\text{conversion}} = 42\text{ mole \% of ethanol}$

Required:  $v_{\text{heat}}$

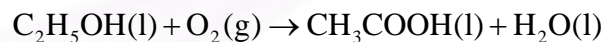
From Appendix D, we are given the enthalpies of formation for both ethanol and acetic acid.

$$\Delta_f H^\circ = -277.6\text{ kJ mol}^{-1}\text{ ethanol(l)}$$

$$\Delta_f H^\circ = -484.3\text{ kJ mol}^{-1}\text{ acetic acid(l)}$$

$$\Delta_f H^\circ = -285.83\text{ kJ mol}^{-1}\text{ water(l)}$$

We can then determine the standard enthalpy change for the reaction:



Note that we also need to use the enthalpy of formation for water which yields;

$$\Delta H^\circ = \Delta_f H^\circ(\text{acetic acid}) + \Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_f H^\circ(\text{ethanol})$$

$$\Delta H^\circ = [(-484.3) + (-285.83) - (-277.6)]\text{ kJ mol}^{-1}$$

$$\Delta H^\circ = (-484.3 - 285.83 + 277.6)\text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -492.53\text{ kJ mol}^{-1}$$

Since the ethanol is fed at a rate of 45.00 kg h<sup>-1</sup>, and only 42% of ethanol is converted, the actual heat evolved during the reaction per hour is defined by (molar mass ethanol is approximately 46.069 g mol<sup>-1</sup>):

$$v_{\text{heat}} = \frac{v_{\text{feed}}}{M} \times v_{\text{conversion}} \times \Delta H^{\circ} = \frac{45.00 \text{ kg h}^{-1}}{0.046\,069 \text{ kg mol}^{-1}} \times (0.42) (-492.53 \text{ kJ mol}^{-1})$$

$$v_{\text{heat}} = -202\,062.49 \text{ kJ h}^{-1}$$

This means that the heat will have to be removed at a rate of 202 MJ h<sup>-1</sup>.

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- 2.32.** **a.** An ice cube at 0 °C weighing 100.0 g is dropped into 1 kg of water at 20 °C. Does all of the ice melt? If not, how much of it remains? What is the final temperature? The latent heat of fusion of ice at 0 °C is 6.025 kJ mol<sup>-1</sup>, and the molar heat capacity of water,  $C_{p,m}$ , is 75.3 J K<sup>-1</sup> mol<sup>-1</sup>.
- b.** Perform the same calculations with 10 ice cubes of the same size dropped into the water. (See Problem 3.33 of Chapter 3 for the calculation of the corresponding entropy changes.)

**Solution:**

Given:  $T = 0\text{ °C}$ ,  $m_{\text{ice}} = 100.0\text{ g}$ ,  $m_{\text{water}} = 1000\text{ g}$ ,  $T_{\text{water}} = 20\text{ °C}$

$$T = 0\text{ °C}, \Delta_{\text{fus}}H = 6.025\text{ kJ mol}^{-1}, C_p = 75.3\text{ J K}^{-1}\text{ mol}^{-1}$$

Required: see above

- a.** Assume that all of the ice melts. The process would then absorb;

$$\frac{m_{\text{ice}} \times \Delta_{\text{fus}}H}{M_{\text{ice}}} = \frac{(100.0\text{ g}) \left( 6.025\text{ kJ mol}^{-1} \right)}{18.02\text{ g mol}^{-1}} = 33.435\text{ 072 214 kJ} = q\text{ absorbed}$$

Let the final temperature be  $T\text{ °C}$ , then we can use the following expression to solve for  $t$ .

$$q = mC_p\Delta T$$

However, since we are determining the value for ten ice cubes, we will use the following:

$$q = mC_p\Delta T$$

$$q = m_{\text{water}}C_p\Delta T$$

$$q = m_{\text{water}}C_p(T_{\text{water}} - T_i)$$

$$33\,435.072\,214\text{ J} = \frac{(1000\text{ g}) \times 75.3\text{ J K}^{-1}\text{ mol}^{-1} \times (20 - T)\text{ K}}{18.02\text{ g mol}^{-1}}$$

$$\frac{(33\,435.072\,214\text{ J})(18.02)}{(1000)(75.3\text{ J})} = (20 - T)$$

$$(20 - T) = 8.001\,328\,038$$

$$T = 20 - 8.001\,328\,038$$

$$T = 11.998\,671\,96 \rightarrow \boxed{T = 12\text{ }^{\circ}\text{C}}$$

Since this value is not below  $0\text{ }^{\circ}\text{C}$ , it means that all of the ice does indeed melt. The final temperature is  $12\text{ }^{\circ}\text{C}$ .

- b.** It is obvious that not all of the ice will melt. (If we assumed that it all melted, we would find that the final temperature would be below  $0\text{ }^{\circ}\text{C}$ .) The final temperature of the water is now  $0\text{ }^{\circ}\text{C}$ , and if we suppose that  $x$  g of the ice melts, we can determine how much ice will remain solid in the water.

$$m_{\text{ice}} \times \Delta_{\text{fus}}H = m_{\text{water}}C_p t \text{ (molecular weight will cancel on both sides)}$$

$$m_{\text{ice}} = \frac{m_{\text{water}}C_p t}{\Delta_{\text{fus}}H}$$

$$m_{\text{ice}} = \frac{(1000\text{ g})(75.3\text{ J K}^{-1}\text{ mol}^{-1})(20\text{ K})}{6\,025\text{ J mol}^{-1}}$$

$$m_{\text{ice}} = 249.958\,506\,2\text{ g}$$

$$m_{\text{ice}} = 250\text{ g}$$

$$10 \times 100\text{ g} - 250 = \boxed{750\text{ grams of ice will remain solid.}}$$

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**2.33.** From the data in Table 2.1 and Appendix D, calculate the enthalpy change in the reaction  

$$\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$$
 at 1000 K.

**Solution:**

Given: Appendix D, Table 2.1,  $T=1000\text{ K}$

Required:  $\Delta H$  for the reaction

All of the values given in Appendix D were taken under the standard conditions of 25 degrees Celsius and 1 bar pressure. For this particular reaction we can see that the enthalpy of formation for carbon dioxide is given by,

$$\Delta_f H^\circ = -393.51 \text{ kJ mol}^{-1}$$

According to the values given in Table 2.1 and using Eq. 2.49 we have the following;

$$\Delta C_{p,m} = \Delta d + \Delta e T + \Delta f T^{-2}$$

$$\Delta d = \sum \Delta d(\text{products}) - \Delta d(\text{reactants})$$

$$\Delta d = \Delta d(\text{CO}_2) - [\Delta d(\text{O}_2) + \Delta d(\text{C})]$$

$$\Delta d = 44.22 - (29.96 + 16.86)$$

$$\Delta d = 44.22 - 29.96 - 16.86$$

$$\Delta d = -2.60 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta e = \sum \Delta e(\text{products}) - \Delta e(\text{reactants})$$

$$\Delta e = \Delta e(\text{CO}_2) - (\Delta e(\text{O}_2) + \Delta e(\text{C}))$$

$$\Delta e = [8.79 - (4.18 + 4.77)] \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$\Delta e = -0.16 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$\Delta f = \sum \Delta f(\text{products}) - \Delta f(\text{reactants})$$

$$\Delta f = \Delta f(\text{CO}_2) - (\Delta f(\text{O}_2) + \Delta f(\text{C}))$$

$$\Delta f = [-8.62 - (-1.67 - 8.54)] \times 10^5 \text{ J K mol}^{-1}$$

$$\Delta f = 1.59 \times 10^5 \text{ J K mol}^{-1}$$

Putting all of these values into Eq. 2.52 we can determine the enthalpy change at 1000 K.

$$\Delta H_m(T_2) = \Delta H_m(T_1) + \Delta d(T_2 - T_1) + \frac{1}{2} \Delta e(T_2^2 - T_1^2) + \Delta f \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\begin{aligned} \Delta H_m(T_2) = & -393\,510 - 2.6(1000 - 298.15) + \frac{1}{2}(-0.16 \times 10^{-3})(1000^2 - 298.15^2) \\ & + (1.59 \times 10^5) \left( \frac{1}{1000} - \frac{1}{298.15} \right) \end{aligned}$$

$$\Delta H_m(T_2) = -395\,781.9871 \text{ J mol}^{-1}$$

$$\boxed{\Delta H_m(1000 \text{ K}) = -395.78 \text{ kJ mol}^{-1}}$$

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**3.34.** From the bond strengths in Table 2.2, estimate the enthalpy of formation of gaseous propane,  $\text{C}_3\text{H}_8$ , using the following additional data:

	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{C}(\text{graphite}) \rightarrow \text{C}(\text{g})$	716.7
$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$	436.0

**Solution:**

Given: Table 2.2, see above

Required:  $\Delta_f H^\circ$

Propane has the molecular formula  $\text{C}_3\text{H}_8$  which means that it contains two carbon-carbon bonds and eight carbon-hydrogen bonds. We can therefore determine the heat of ionization by using the following;

$$q_{\text{atomization}} = \sum (\# \text{ bonds of type } n) (\text{bond enthalpy of type } n)$$

$$q_{\text{atomization}} = [(2 \times 348) + (8 \times 413)] \text{ kJ mol}^{-1}$$

$$q_{\text{atomization}} = 4000 \text{ kJ mol}^{-1}$$

Now we need to determine the correct and balanced equation for the reaction which forms propane. After this, we must also determine the reactions for the formation of each species involved.



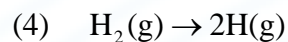
$$\Delta_f H^\circ = -4000 \text{ kJ mol}^{-1}$$



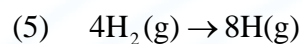
given that  $\Delta_f H^\circ = 716.7 \text{ kJ mol}^{-1}$  therefore,



$$\Delta_f H^\circ = 2150.1 \text{ kJ mol}^{-1}$$

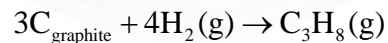
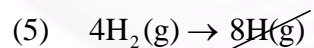
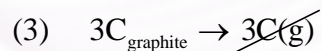
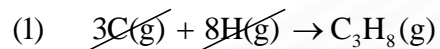


given that  $\Delta_f H^\circ = 436.0 \text{ kJ mol}^{-1}$  therefore,



$$\Delta_f H^\circ = 1744 \text{ kJ mol}^{-1}$$

When we add equations 1, 3 and 5, we obtain the desired reaction:



Doing the same thing for the enthalpies of formation we obtain,

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = \Delta_f H^\circ(\text{Eq.1}) + \Delta_f H^\circ(\text{Eq.3}) + \Delta_f H^\circ(\text{Eq.5})$$

$$\Delta H^\circ = (-4000 + 2150.1 + 1744) \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ(\text{graphite}) = -105.9 \text{ kJ mol}^{-1}}$$

The agreement with experiment,  $-103.8 \text{ kJ mol}^{-1}$  is relatively good.

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**2.35.** A sample of sucrose,  $C_{12}H_{22}O_{11}$  weighing 0.1328 g, was burned to completion in a bomb calorimeter at 25 °C, and the heat evolved was measured to be 2186.0 J.

**a.** Calculate  $\Delta_c U_m$  and  $\Delta_c H_m$  for the combustion of sucrose.

**b.** Use data in Appendix D to calculate  $\Delta_f H_m$  for the formation of sucrose.

**Solution:**

Given:  $m_{\text{sucrose}} = 0.1328 \text{ g}$ ,  $T = 25 \text{ °C}$ , heat =  $q_{V,m} = 2186.0 \text{ J}$ , Appendix D

Required:  $\Delta_c U_m$ ,  $\Delta_c H_m$ ,  $\Delta_f H_m$

**a.** Remember that when using a bomb calorimeter, we are working under constant volume. With that said, the heat evolved per gram will be;

$$q_{V,m} = \frac{q_V}{m}$$

$$q_{V,m} = \frac{2186.0 \text{ J}}{0.1328 \text{ g}}$$

$$q_{V,m} = 16\,460.843\,37 \text{ J g}^{-1}$$

We can now use this information in order to determine the change in internal energy which is given by;

$$\Delta_c U^\circ = -q_{V,m}$$

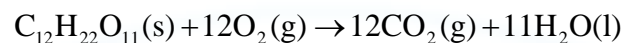
when working under constant volume conditions. Using the molar mass for sucrose (approximately  $342.3 \text{ g mol}^{-1}$ ) we can determine the change in internal energy per mole of substance combusted.

$$\Delta_c U_m = -q_{V,m} \times M_{\text{sucrose}}$$

$$\Delta_c U_m = (-16\,460.843\,37 \text{ J g}^{-1})(342.3 \text{ g mol}^{-1})$$

$$\boxed{\Delta_c U_m = -5\,635 \text{ kJ mol}^{-1}}$$

The balanced reaction for the combustion of sucrose is given by,



The change in the number of moles for the gaseous species is therefore

$$\Delta n = \sum n_{\text{products}} - n_{\text{reactants}}$$

$$\Delta n = 12 - 12$$

$$\Delta n = 0$$

According to Eq. 2.41 we can then say that;

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta nRT = \Delta(PV)$$

since  $\Delta nRT = 0$  then  $\Delta(PV) = 0$

$$\Delta H = \Delta U$$

$$\boxed{\Delta H = -5\,635 \text{ kJ mol}^{-1}}$$

- b.** For the formation of sucrose, we can use the same reaction given above for combustion but in reverse. Using Hess' Law which states:

$$\Delta_f H_m = \sum \Delta_f H_m(\text{products}) - \Delta_f H_m(\text{reactants})$$

We can rearrange and make the appropriate substitutions using information given in Appendix D to obtain,

$$\Delta_f H_m = \sum \Delta_f H_m(\text{products}) - \Delta_f H_m(\text{reactants})$$

$$\Delta_f H_m = 12\Delta_f H_m(\text{CO}_2, \text{g}) + 11\Delta_f H_m(\text{H}_2\text{O}, \text{l}) - \Delta_f H_m(\text{sucrose})$$

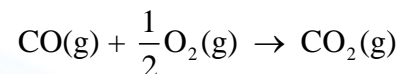
$$\Delta_f H_m = [(12 \times -393.51) + (11 \times -285.83) - (-5\,635)] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_f H_m = -2\,231 \text{ kJ mol}^{-1}}$$

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**2.36.** The value of  $\Delta H^\circ$  for the reaction



is  $-282.97 \text{ kJ mol}^{-1}$  at 298 K. Calculate  $\Delta U^\circ$  for the reaction.

**Solution:**

Given:  $\Delta H^\circ = -282.97 \text{ kJ mol}^{-1}$ ,  $T = 298 \text{ K}$

Required:  $\Delta U^\circ$

Since we have been given the standard change in enthalpy, we can simply use Eq. 2.41 and rearrange in order to determine the standard change in internal energy. First, we must determine the change in moles for the gaseous species.

$$\Delta n = \sum \Delta n(\text{products}) - \Delta n(\text{reactants})$$

$$\Delta n = 1\text{CO}_2 - (1\text{CO} + \frac{1}{2}\text{O}_2)$$

$$\Delta n = 1 - 1.5$$

$$\Delta n = -\frac{1}{2}$$

According to Eq. 2.41:

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta nRT = \Delta(PV) \text{ and therefore}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT$$

$$\Delta U^\circ = (-282\,970 \text{ J mol}^{-1}) - (-0.5 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})$$

$$\Delta U^\circ = -281\,730.5159 \text{ J mol}^{-1}$$

$$\boxed{\Delta U^\circ = -281.73 \text{ kJ mol}^{-1}}$$

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- 2.37.** One mole of an ideal gas initially at 10.00 bar and 298.0 K is allowed to expand against a constant external pressure of 2.000 bar to a final pressure of 2.000 bar. During this process, the temperature of the gas falls to 253.2 K. We wish to construct a reversible path connecting these initial and final steps as a combination of a reversible isothermal expansion followed by a reversible adiabatic expansion. To what volume should we allow the gas to expand isothermally so that subsequent adiabatic expansion is guaranteed to take the gas to the final state? Assume that  $C_{V,m} = \frac{3}{2}R$ .

**Solution:**

Given: Ideal Gas:  $P_i = 10.00$  bar,  $T_i = 298.0$  K,  $P_{ext} = 2.00$  bar,  $P_f = 2.00$  bar,  $T_f = 253.2$  K

Required:  $V_i$

It should be noted that we are required to find the intersection of the isotherm that passes through the *initial* state and the adiabat that passes through the *final* state. We will call this point  $(P_i, V_i)$  and the temperature of the isotherm will be  $T_i$ .

Recall that for adiabatic processes we use Eq. 290 which states that:

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma-1}$$

We must first determine the value for  $\gamma$  in order to solve the above expression. Remember that it can be found using Eq. 2.88 and knowing that for an Ideal Gas,

$$\gamma = \frac{C_{P,m}}{C_{V,m}}$$

$$C_{P,m} - C_{V,m} = R$$

$$C_{V,m} = \frac{3}{2}R \text{ and therefore,}$$

$$C_{P,m} = \frac{3}{2}R + R$$

$$\gamma = \frac{\left(\frac{3}{2}R + R\right)}{\left(\frac{3}{2}R\right)} = \frac{\frac{5}{2} \cancel{R}}{\frac{3}{2} \cancel{R}}$$

$$\gamma = \frac{5}{\cancel{2}} \times \frac{\cancel{2}}{3}$$

$$\gamma = \frac{5}{3}$$

$$\gamma - 1 = \frac{2}{3}$$

The final volume can be solved for using the Ideal Gas Law.

$$PV = nRT$$

$$V_f = \frac{RT_f}{P_f}$$

$$V_f = \frac{(0.08315 \text{ dm}^3 \cancel{\text{ bar}} \cancel{\text{ K}}^{-1} \text{ mol}^{-1})(253.2 \cancel{\text{ K}})}{2.0 \cancel{\text{ bar}}}$$

$$V_f = 10.526 \text{ 79 dm}^3$$

Now we are able to rearrange Eq. 2.90 in order to solve for the initial volume.

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma-1}$$

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\frac{2}{3}} \rightarrow \left( \frac{T_f}{T_i} \right)^{\frac{3}{2}} = \frac{V_i}{V_f}$$

$$V_i = V_f \left( \frac{T_f}{T_i} \right)^{\frac{3}{2}}$$

$$V_i = (10.52 \text{ 679 dm}^3) \left( \frac{253.2 \text{ K}}{298.0 \text{ K}} \right)^{\frac{3}{2}}$$

$$V_i = 8.244 \text{ 553 018 dm}^3$$

$$\boxed{V_i = 8.245 \text{ dm}^3}$$

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- 2.38.** Two moles of oxygen gas, which can be regarded as ideal with  $C_p = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$  (independent of temperature), are maintained at 273 K in a volume of  $11.35 \text{ dm}^3$ .
- What is the pressure of the gas?
  - What is  $PV$ ?
  - What is  $C_v$ ?

**Solution:**

Given: Oxygen Gas:  $C_p = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 273 \text{ K}$ ,  $V = 11.35 \text{ dm}^3$

Required:  $P_{\text{O}_2}$ ,  $PV$ ,  $C_v$

- a.** One mole of oxygen gas in a volume of  $22.7 \text{ dm}^3$  and at 273 K exerts a pressure of 1 bar. If we make the necessary adjustments to account for the difference in volume (one half the volume means twice the pressure) the gas would exert a 2 bar pressure. We must now account for the number of moles of gas (of which there are two) which would bring the pressure up to 4 bar.

$$\boxed{P_{\text{O}_2} = 4 \text{ bar}}$$

- b.** Now we can determine the amount of  $PV$  work done in addition to the heat capacity under constant volume.

$$PV = (4 \text{ bar})(11.35 \text{ dm}^3)$$

$$PV = 45.4 \text{ bar dm}^3$$

$$\text{since } 1 \text{ bar dm}^3 = 100 \text{ J}$$

$$45.4 \text{ bar dm}^3 = 4540 \text{ J} = 4.540 \text{ kJ}$$

$$\boxed{PV = 4.540 \text{ kJ}}$$

- c.** For an ideal gas we know that,

$$C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P \quad (\text{Eq. 2.117})$$

Since, for an ideal gas  $\left( \frac{\partial U}{\partial V} \right)_T = 0$ , this can be simplified to Eq. 2.118:

$$C_p - C_v = P \left( \frac{\partial V}{\partial T} \right)_p$$

For 1 mole of an ideal gas, we already know that  $PV_m = RT$  and therefore,  $\left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{P}$

which produces the following expression:

$$C_{p,m} - C_{v,m} = R \quad (\text{Eq. 2.119})$$

And rearranging for  $C_v$  we get,

$$C_{p,m} - C_{v,m} = R$$

$$C_{v,m} = C_{p,m} - R$$

$$C_{v,m} = 29.4 \text{ J K}^{-1} \text{ mol}^{-1} - 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{v,m} = 21.0855 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{C_{v,m} = 21.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**2.39.** Suppose that the gas in Problem 2.38 is heated reversibly to 373 K at *constant volume*:

- a. How much work is done on the system?
- b. What is the increase in internal energy,  $\Delta U$ ?
- c. How much heat was added to the system?
- d. What is the final pressure?
- e. What is the final value of  $PV$ ?
- f. What is the increase in enthalpy,  $\Delta H$ ?

**Solution:**

Given: Oxygen (Problem 2.38):  $T_i = 273 \text{ K}$ ,  $T_f = 373 \text{ K}$

Required:  $w$ ,  $\Delta U_m$ ,  $q_{added}$ ,  $P_f$ ,  $PV$ ,  $\Delta H_m$

- a. A very important process is the compression of an ideal gas (such as the oxygen in Problem 2.38) under constant volume. This process is illustrated in Figure 2.6b.

It is important to remember that for an ideal gas at constant volume,

$$q_{V,m} = \int_{T_1}^{T_2} C_{V,m} dT$$

$$q_{V,m} = C_{V,m} (T_2 - T_1)$$

This also means that for an ideal gas,

$$\Delta U_m = C_{V,m} (T_2 - T_1)$$

$$\Delta H_m = C_{P,m} (T_2 - T_1)$$

The work *done on* the system in a reversible compression of one mole of gas is given by the following,

$$w_{rev} = - \int_{V_{m,1}}^{V_{m,2}} P dV \quad (\text{Eq. 2.70})$$

Since the pressure is varying, we must express this in terms of  $V_m$  by using the Ideal Gas Law for a single mole.

$$w_{\text{rev}} = -\int_{V_{m,1}}^{V_{m,2}} P dV$$

$$PV_m = RT$$

$$w_{\text{rev}} = -\int_{V_{m,1}}^{V_{m,2}} \frac{RT}{V_m} dV$$

$$w_{\text{rev}} = -RT \ln(V) \Big|_{V_{m,1}}^{V_{m,2}}$$

$$w_{\text{rev}} = -RT \ln \left( \frac{V_{m,2}}{V_{m,1}} \right)$$

This can also be written as;

$$w_{\text{rev}} = RT \ln \left( \frac{V_{m,1}}{V_{m,2}} \right) \text{ which then gives,}$$

$$w_{\text{rev}} = (8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1})(273 \cancel{\text{K}}) \ln \left( \frac{1}{1} \right)$$

$$\boxed{w_{\text{rev}} = 0}$$

**b.** Now we can use the first two expressions given above in order to determine the change in internal energy and change in enthalpy.

$$\Delta U_m = nC_{V,m}(T_2 - T_1)$$

$$\Delta U_m = (2 \cancel{\text{mol}})21.1 \text{ J } \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}} (373 - 273) \cancel{\text{K}}$$

$$\Delta U_m = 4220 \text{ J}$$

$$\boxed{\Delta U_m = 4.22 \text{ kJ}}$$

**c.** Recall that at constant volume, the change in internal energy is equivalent to the amount of heat *added* to the system and therefore,

$$q_{\text{added}} = \Delta U_m$$

$$\boxed{q_{\text{added}} = 4.22 \text{ kJ}}$$

d. Knowing that  $\frac{T_2}{T_1} = \frac{\lim_{P \rightarrow 0}(PV)_2}{\lim_{P \rightarrow 0}(PV)_1}$  from Chapter 1 (Eq. 1.22), we can solve for the final pressure.

$$P_2 = \frac{P_1 T_2}{T_1}$$

$$P_2 = \frac{4 \text{ bar} \times 373.15 \text{ K}}{273.15 \text{ K}}$$

$$P_2 = 5.464 \ 396 \ 852 \text{ bar}$$

Since 1 bar =  $10^5$  Pa then we can say that,

$$P_f = 5.464 \ 396 \ 852 \text{ bar} \left( 10^5 \text{ Pa bar}^{-1} \right)$$

$$P_f = 546 \ 439.6852 \text{ Pa}$$

$$\boxed{P_f = 5.46 \text{ kPa}}$$



e.

$$PV = P_2 V_2$$

$$PV = (5.464\,396\,852\text{ bar})(11.35\text{ dm}^3)$$

$$PV = 62.020\,904\,27\text{ bar dm}^3$$

$$1\text{ bar} = 10^5\text{ Pa and } 1\text{ atm} = 1.01325 \times 10^5\text{ Pa}$$

$$PV = (62.020\,904\,27 \cancel{\text{bar}}\text{ dm}^3) \left( 10^5 \cancel{\text{Pa}} \cancel{\text{bar}^{-1}} \right) \left( \frac{1\text{ atm}}{1.01325 \times 10^5 \cancel{\text{Pa}}} \right)$$

$$PV = 61.209\,873\,45\text{ atm dm}^3$$

and since,  $1\text{ atm dm}^3 = 101.325\text{ J}$  then,

$$PV = 61.209\,873\,45 \cancel{\text{atm dm}^3} \left( \frac{101.325\text{ J}}{1 \cancel{\text{atm dm}^3}} \right)$$

$$PV = 6202.090\,427\text{ J}$$

$$\boxed{PV = 6.20\text{ kJ}}$$

f. The change in enthalpy can now be determined.

$$\Delta H_m = n C_{p,m} (T_2 - T_1)$$

$$\Delta H_m = (2 \cancel{\text{mol}})(29.4\text{ J } \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}})(373.15 - 273.15) \cancel{\text{K}}$$

$$\Delta H_m = 5880\text{ J}$$

$$\boxed{\Delta H_m = 5.88\text{ kJ}}$$

Alternately, we can determine the enthalpy change using Eq. 2.41 which yields approximately the same answer.

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**2.40.** Suppose that the gas in Problem 2.38 is heated reversibly to 373 K at *constant pressure*.

- a. What is the final volume?
- b. How much work is done on the system?
- c. How much heat is supplied to the system?
- d. What is the increase in enthalpy?
- e. What is the increase in internal energy?

**Solution:**

Given: Oxygen (problem 2.38):  $T_i = 273 \text{ K}$ ,  $T_f = 373 \text{ K}$

Required:  $V_f$ ,  $w_{\text{rev}}$  (on system),  $q_{P,m}$ ,  $\Delta H_{P,m}$ ,  $\Delta U_{P,m}$

- a. The pressure-volume relationship for the reversible compression of an ideal gas at constant pressure can be found in Figure 2.6a. Remember from Chapter 1 that we have,

$$\frac{T_2}{T_1} = \frac{\lim_{P \rightarrow 0} (PV)_2}{\lim_{P \rightarrow 0} (PV)_1}$$

$$\frac{T_2}{T_1} = \frac{V_2}{V_1}$$

$$V_2 = \frac{V_1 T_2}{T_1}$$

$$V_f = \frac{11.35 \text{ dm}^3 \times 373.15 \text{ K}}{273.15 \text{ K}}$$

$$\boxed{V_f = 15.5 \text{ dm}^3}$$

- b. The work *done on* the system for one mole can be defined by,

$$w_{\text{rev}} = -\int_{V_{m,1}}^{V_{m,2}} P_1 dV = -P_1(V_{m,2} - V_{m,1})$$

$$w_{\text{rev}} = P_1(V_{m,1} - V_{m,2})$$

This expression is true whether the gas we are working with is ideal or not. If we use the Ideal Gas Law, we can get,

$$w_{\text{rev}} = P_1 \left( \frac{RT_1}{P_1} - \frac{RT_2}{P_1} \right)$$

Which simplifies to the following;

$$w_{\text{rev}} = R(T_1 - T_2)$$

For two moles of oxygen:

$$w_{\text{rev}} = (2 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 - 373.15) \text{ K}$$

$$w_{\text{rev}} = -1662.9 \text{ J}$$

However, since the work is being done ON the system, the value will be positive.

$$\boxed{w_{\text{rev}} = 1.66 \text{ kJ}}$$

c. The heat absorbed by the system during such a process is given by;

$$q_{P,m} = \int_{T_1}^{T_2} C_{P,m} dT \quad (\text{Eq. 2.57})$$

Now, since the pressure is constant, the heat capacity will be independent of temperature and this integral will simplify to:

$$q_{P,m} = C_{P,m} (T_2 - T_1)$$

For two moles of oxygen:

$$q_{P,m} = nC_{P,m} (T_2 - T_1)$$

$$q_{P,m} = (2 \text{ mol})(29.4 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 - 273.15) \text{ K}$$

$$q_{P,m} = 5880 \text{ J}$$

$$\boxed{q_{P,m} = 5.88 \text{ kJ}}$$

- d. According to Eq. 2.59, the change in enthalpy is equal to the amount of heat supplied to the system when the work is done under constant pressure.

$$\Delta H_{P,m} = C_{P,m}(T_2 - T_1)$$

$$\Delta H_{P,m} = q_{P,m}$$

$$\boxed{\Delta H_{P,m} = 5.88 \text{ kJ}}$$

- e. We can now use Eq. 2.41 and rearrange it in order to solve for the change in internal energy.

$$\Delta H_{P,m} = \Delta U_{P,m} + \Delta(PV)$$

$$\Delta H_{P,m} = \Delta U_{P,m} + w_{rev}$$

$$\Delta U_{P,m} = \Delta H_{P,m} - w_{rev}$$

$$\Delta U_{P,m} = (5.88 - 1.66) \text{ kJ}$$

$$\boxed{\Delta U_{P,m} = 4.22 \text{ kJ}}$$

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- 2.41.** Suppose that the gas in Problem 2.38 is reversibly compressed to *half its volume* at constant temperature (273 K).
- What is the change in  $U$ ?
  - What is the final pressure?
  - How much work is done on the system?
  - How much heat flows out of the system?
  - What is the change in  $H$ ?

**Solution:**

Given: Oxygen (Problem 2.38):  $T_i = 273\text{ K}$ ,  $T_f = 373\text{ K}$

Required:  $\Delta U_m$ ,  $P_f$ ,  $w_{\text{rev}}$ ,  $q_{\text{outflow}}$ ,  $\Delta H_m$

- a.** Another process of great importance is the compression of an ideal gas along an isotherm. This means that the process is occurring at constant temperature. An illustration of such a process is given in Figure 2.6c. We should note that for an ideal gas undergoing compression at constant temperature,

$\Delta H_m = 0$  and

$$\boxed{\Delta U_m = 0}$$

- b.** The final pressure can be found using  $P_1V_1 = P_2V_2$  and rearranging to get,

$$P_2 = \frac{P_1V_1}{V_2}$$

$$P_f = \frac{(4\text{ bar})(11.35\text{ dm}^3)}{5.675\text{ dm}^3}$$

$$\boxed{P_f = 8\text{ bar}}$$

- c.** The work done on the system in a reversible compression is given by,

$$w_{\text{rev}} = -\int_{V_{m,1}}^{V_{m,2}} PdV$$

Since the pressure is varying, we must express this equation in terms of  $V_m$  by making use of the Ideal Gas Law.

$$w_{\text{rev}} = - \int_{V_{m,1}}^{V_{m,2}} \frac{nRT}{V_m} dV$$

$$w_{\text{rev}} = -nRT \ln(V) \Big|_{V_{m,1}}^{V_{m,2}}$$

$$w_{\text{rev}} = -nRT \ln \left( \frac{V_{m,2}}{V_{m,1}} \right)$$

$$w_{\text{rev}} = nRT \ln \left( \frac{V_{m,1}}{V_{m,2}} \right)$$

$$w_{\text{rev}} = (2 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K}) \ln \left( \frac{11.35}{5.675} \right)$$

$$w_{\text{rev}} = 3146.69 \text{ J}$$

$$\boxed{w_{\text{rev}} = 3.15 \text{ kJ}}$$

- d.** The amount of heat flowing out of the system is equal in magnitude but opposite in sign to the amount of work done ON the system. This is true because this is the only way to keep the temperature of the system constant.

$$w_{\text{rev}} = -q_{\text{outflow}}$$

$$\boxed{q_{\text{outflow}} = -3.15 \text{ kJ}}$$

- e.** Since there is no temperature change,  $\boxed{\Delta H = 0}$

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- 2.42.** With the temperature maintained at 0 °C, 2 mol of an ideal gas are allowed to expand against a piston that supports 2 bar pressure. The initial pressure of the gas is 10 bar and the final pressure 2 bar.
- How much energy is transferred to the surroundings during the expansion?
  - What is the change in the internal energy and the enthalpy of the gas?
  - How much heat has been absorbed by the gas?

**Solution:**

Given: Ideal Gas:  $T = 0\text{ °C}$ ,  $n = 2\text{ mol}$ ,  $P_{\text{piston}} = 2.0\text{ bar}$ ,  $P_i = 10\text{ bar}$ ,  $P_f = 2\text{ bar}$

Required:  $w(\text{by gas})$ ,  $\Delta U$ ,  $\Delta H$ ,  $q(\text{absorbed})$

- We are given that we are making changes to a system under constant temperature. It is first important to determine the change in volume because we know that there is only  $PV$  work involved.

$$PV = nRT$$

$$V_i = \frac{nRT}{P_i}$$

$$V_i = \frac{(2\text{ mol})(0.083\,144\,72\text{ bar dm}^3\text{ K}^{-1}\text{ mol}^{-1})(273.15\text{ K})}{10\text{ bar}}$$

$$V_i = 4.54\text{ dm}^3$$

Now we can find the final volume and hence, the volume change.

$$P_i V_i = P_f V_f$$

$$V_f = \frac{P_i V_i}{P_f}$$

$$V_f = \frac{(10 \text{ bar})(4.54 \text{ dm}^3)}{2 \text{ bar}}$$

$$V_f = 22.71 \text{ dm}^3$$

$$\Delta V = V_f - V_i$$

$$\Delta V = (22.70 - 4.54) \text{ dm}^3$$

$$\Delta V = 18.16 \text{ dm}^3$$

Now the work done by the gas is given by pressure multiplied by the change in volume;

$$w = P \Delta V$$

$$w = (2 \text{ bar})(18.16 \text{ dm}^3)$$

$$w = 36.32 \text{ bar dm}^3$$

$$w = (36.32 \text{ bar dm}^3) \left( 10^5 \text{ Pa bar}^{-1} \right) \left( \frac{1 \text{ atm}}{1.01325 \times 10^5 \text{ Pa}} \right)$$

$$w = 35.845 \text{ atm dm}^3$$

Since  $1 \text{ atm dm}^3 = 101.325 \text{ J}$  then,

$$w = (35.845 \text{ atm dm}^3) \left( \frac{101.325 \text{ J}}{1 \text{ atm dm}^3} \right)$$

$$\boxed{w = 3632 \text{ J}}$$

The amount of work done by the gas will be equal to the amount of heat transferred to the surroundings because the temperature of the system needs to remain constant.



b. Remember that at constant temperature,

$$\Delta U_m = 0$$

$$\Delta H_m = 0$$

c. The amount of heat absorbed by the gas will be equal to the amount of work done.

$$q_{\text{absorbed}} = 3632 \text{ J}$$

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- 2.43.** Suppose that the gas in Problem 2.42 is allowed to expand *reversibly* and *isothermally* from the initial pressure of 10 bar to the final pressure of 2 bar.
- How much work is done by the gas?
  - What are  $\Delta U$  and  $\Delta H$ ?
  - How much heat is absorbed by the gas?

**Solution:**

Given: (problem 2.42):  $P_i = 10$  bar,  $P_f = 2$  bar

Required:  $w$ (by gas),  $\Delta U$ ,  $\Delta H$ ,  $q_{\text{absorbed}}$

- a.** We are again working under conditions of constant temperature so we can solve this problem in the same way that we have done before. We can determine the amount of work done by the gas by using the volume change found in the previous problem.

$$V_f = 22.71 \text{ dm}^3$$

$$V_i = 4.54 \text{ dm}^3$$

$$w_{\text{rev}} = nRT \ln \frac{V_f}{V_i}$$

$$w_{\text{rev}} = (2 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (273.15 \text{ K}) \ln \left( \frac{22.71}{4.54} \right)$$

$$w_{\text{rev}} = 7312.407 \text{ J}$$

$$\boxed{w_{\text{rev}} = 7.31 \text{ kJ}}$$

- b.** Remember we are still working under constant temperature which means that,

$$\boxed{\Delta U_m = 0}$$

$$\boxed{\Delta H_m = 0}$$

- c.** The amount of heat absorbed by the gas will be equal to the amount of work done in order to keep the temperature constant.

$$\boxed{q = 7.31 \text{ kJ}}$$

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- 2.44.** A sample of hydrogen gas, which may be assumed to be ideal, is initially at 3.0 bar pressure and a temperature of 25.0 °C, and has a volume of 1.5 dm<sup>3</sup>. It is expanded reversibly and adiabatically until the volume is 5.0 dm<sup>3</sup>. The heat capacity  $C_P$  of H<sub>2</sub> is 28.80 J K<sup>-1</sup> mol<sup>-1</sup> and may be assumed to be independent of temperature.
- Calculate the final pressure and temperature after the expansion.
  - Calculate  $\Delta U$  and  $\Delta H$  for the process.

**Solution:**

Given: Hydrogen gas:  $P_i = 3.0$  bar,  $T_i = 25$  °C,  $V_i = 1.5$  dm<sup>3</sup>,  $V_f = 5.0$  dm<sup>3</sup>,

$$C_p = 28.80 \text{ J K}^{-1} \text{ mol}^{-1}$$

Required:  $P_f$ ,  $T_f$ ,  $\Delta U$ ,  $\Delta H$

Another process to consider is the compression or expansion of an ideal gas contained in a vessel whose walls are perfectly insulated. This means that heat cannot pass through them. Such processes are called adiabatic. The pressure-volume relationship for this type of process is given in Figure 2.6d.

- Since the work is performed on the gas in order to compress it and no heat can leave the system, the final temperature must be higher than the initial temperature.

Using the value of  $C_P$ , we can determine  $C_V$  according to Eq. 2.119,

$$C_{P,m} - C_{V,m} = R$$

$$C_{V,m} = C_{P,m} - R$$

$$C_{V,m} = 28.80 \text{ J K}^{-1} \text{ mol}^{-1} - 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{V,m} = 20.4855 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note that the ratio of  $C_P$  to  $C_V$  is often written as,

$$\gamma = \frac{C_{P,m}}{C_{V,m}}$$

We can now derive a version of Boyle's Law for this adiabatic process.

$$P_i V_i^\gamma = P_f V_f^\gamma$$

We can use this first to determine the final pressure for the system.

$$P_f = \frac{P_i V_i^\gamma}{V_f^\gamma}$$

$$P_f = P_i \left( \frac{V_i}{V_f} \right)^\gamma$$

$$P_f = (3.0 \text{ bar}) \left( \frac{1.5 \text{ dm}^3}{5 \text{ dm}^3} \right)^\gamma$$

$$\gamma = \frac{C_{P,m}}{C_{V,m}} = \frac{28.80 \text{ J K}^{-1} \text{ mol}^{-1}}{20.4855 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\gamma = 1.405872446$$

$$P_f = (3.0 \text{ bar}) \left( \frac{1.5 \text{ dm}^3}{5 \text{ dm}^3} \right)^{1.405872446}$$

$$P_f = 0.552103415$$

$$\boxed{P_f = 0.552 \text{ bar}}$$

Using Eq. 2.90 it is possible to determine the final temperature.

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

Now rearrange to get,

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 = (298.15 \text{ K}) \left( \frac{1.5 \text{ dm}^3}{5 \text{ dm}^3} \right)^{\gamma-1}$$

$$\gamma = 1.40587$$

$$T_2 = (298.15 \text{ K}) \left( \frac{1.5 \text{ dm}^3}{5 \text{ dm}^3} \right)^{0.405872446}$$

$$T_2 = 182.9624066 \text{ K}$$

$$\boxed{T_2 = 183.0 \text{ K}}$$

**b.** Both  $U$  and  $H$  remain unchanged as we move along the  $T_1$  isothermal and the same is true for the  $T_2$  isothermal. The changes in  $U$  and  $H$  can be found using Eq. 2.29 and Eq. 2.31 respectively.

$$\Delta U_m = C_{V,m} (T_2 - T_1)$$

$$\Delta U_m = (20.49 \text{ J K}^{-1} \text{ mol}^{-1}) (182.9624066 - 298.15) \text{ K}$$

$$\Delta U_m = -2360.193789 \text{ J mol}^{-1}$$

Now we need to determine the number of moles of hydrogen using the Ideal Gas Law.

$$PV = nRT$$

$$n_{\text{H}_2} = \frac{PV}{RT}$$

$$n_{\text{H}_2} = \frac{(3.0 \text{ bar})(1.5 \text{ dm}^3)}{(0.08314472 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$n_{\text{H}_2} = 0.18152775 \text{ mol}$$

$$\Delta U_m = (0.181\,527\,75 \cancel{\text{mol}}) (-2360.193\,789 \text{ J } \cancel{\text{mol}^{-1}})$$

$$\Delta U_m = -428.440\,668\,4$$

$$\boxed{\Delta U_m = -428.4 \text{ J}}$$

Likewise, for the change in enthalpy we get,

$$\Delta H_m = C_{P,m} (T_2 - T_1)$$

$$\Delta H_m = (28.80 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1}) (182.962\,406\,6 - 298.15 \text{ K})$$

$$\Delta H_m = -3317.402\,69 \text{ J mol}^{-1}$$

$$\Delta H_m = (0.181\,527\,75 \cancel{\text{mol}}) (-3317.402\,69 \text{ J } \cancel{\text{mol}^{-1}})$$

$$\Delta H_m = -602.200\,646\,1 \text{ J}$$

$$\boxed{\Delta H_m = -602.2 \text{ J}}$$

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- 2.45.** Initially 0.1 mol of methane is at 1 bar pressure and 80 °C. The gas behaves ideally and the value of  $C_p/C_v$  is 1.31. The gas is allowed to expand reversibly and adiabatically to a pressure of 0.1 bar.
- What are the initial and final volumes of the gas?
  - What is the final temperature?
  - Calculate  $\Delta U$  and  $\Delta H$  for the process.

**Solution:**

Given: Ideal Gas:  $n_{\text{methane}} = 0.1 \text{ mol}$ ,  $P_i = 1 \text{ bar}$ ,  $T = 80^\circ\text{C}$ ,  $\frac{C_p}{C_v} = 1.31$ ,  $P_f = 0.1 \text{ bar}$

Required:  $V_i$ ,  $V_f$ ,  $T_f$ ,  $\Delta U$ ,  $\Delta H$

Another process to consider is the compression or expansion of an ideal gas contained in a vessel whose walls are perfectly insulated. This means that heat cannot pass through them. These processes are called adiabatic. The pressure-volume relationship for this type of process is given in Figure 2.6d.

We may start by finding the initial volume by using the Ideal Gas Law:

$$P_i V_i = nRT$$

$$V_i = \frac{nRT}{P_i}$$

$$V_i = \frac{(0.1 \text{ mol})(0.08314472 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(353.15 \text{ K})}{1 \text{ bar}}$$

$$V_i = 2.936255787 \text{ dm}^3$$

$$\boxed{V_i = 2.936 \text{ dm}^3}$$

We can now make use of Eq. 2.92 which states that,

$$\frac{P_f}{P_i} = \left( \frac{V_f}{V_i} \right)^\gamma$$

This can easily be rearranged in order to solve for the final volume since we are given both the initial and final pressures in addition to  $\gamma$ .

$$V_f = V_i \left( \frac{P_i}{P_f} \right)^{\frac{1}{\gamma}}$$

$$V_f = (2.936\,255\,787\,\text{dm}^3) \left( \frac{1\,\cancel{\text{bar}}}{0.1\,\cancel{\text{bar}}} \right)^{\frac{1}{\gamma}}$$

$$\gamma = \frac{C_{P,m}}{C_{V,m}} = 1.31$$

$$\frac{1}{\gamma} = \frac{1}{1.31} = 0.763\,358\,778$$

$$V_f = (2.936\,\text{dm}^3) \left( \frac{1\,\cancel{\text{bar}}}{0.1\,\cancel{\text{bar}}} \right)^{0.763\,358\,778}$$

$$V_f = 17.027\,569\,61\,\text{dm}^3$$

$$\boxed{V_f = 17.026\,\text{dm}^3}$$

Using Eq. 2.91 it is possible to solve for the final temperature of the system,

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} \quad (\text{Eq. 2.91})$$



$$T_f = \frac{T_i P_f V_f}{P_i V_i}$$

$$T_f = \frac{(353.15 \text{ K})(0.1 \text{ bar})(17.027 569 61 \text{ dm}^3)}{(1 \text{ bar})(2.936 255 787 \text{ dm}^3)}$$

$$T_f = 204.794 334 6 \text{ K}$$

$$\boxed{T_f = 204.8 \text{ K}}$$

Since we are given both  $C_{P,m}$  and  $C_{V,m}$  (in ratio form) for the system, and  $\Delta U$  and  $\Delta H$  are defined in the following manner,

$$\Delta U = C_V (T_f - T_i)$$

$$\Delta H = C_P (T_f - T_i)$$

We can use these equations (Eq.2.95 and 2.96) in order to solve for the final wanted variables. However, since we are only given then ratio, we need to use Eq. 2.119 (to determine each unique value) which states that,

$$C_{P,m} - C_{V,m} = R \text{ and therefore,}$$

$$C_{P,m} - C_{V,m} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\frac{C_{P,m}}{C_{V,m}} = 1.31$$

$$\frac{C_{P,m}}{C_{V,m}} - 1 = 0.31$$

$$\text{therefore, } C_{P,m} - C_{V,m} = 0.31C_{V,m}$$

$$\text{since } C_{P,m} - C_{V,m} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

then we get:

$$C_{V,m} = \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{0.31} = 26.820 \ 967 \ 74 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{P,m} = C_{V,m} (0.31) + C_{V,m} = 35.135 \ 467 \ 74 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta U_m = C_{V,m} (T_f - T_i)$$

$$\Delta U_m = (26.820 \ 967 \ 74 \text{ J K}^{-1} \text{ mol}^{-1})(204.794 \ 334 \ 6 \text{ K} - 353.15 \text{ K})$$

$$\Delta U_m = -3979.042 \ 516 \text{ J mol}^{-1}$$

$$\Delta U = n\Delta U_m$$

$$\Delta U = (0.1 \text{ mol})(-3979.042 \ 516 \text{ J mol}^{-1})$$

$$\Delta U = -397.904 \ 251 \ 6 \text{ J}$$

$$\boxed{\Delta U = -397.9 \text{ J}}$$

$$\Delta H_m = C_{P,m} (T_f - T_i)$$

$$\Delta H_m = (35.135 \ 467 \ 74 \text{ J K}^{-1} \text{ mol}^{-1})(204.794 \ 334 \ 6 \text{ K} - 353.15 \text{ K})$$

$$\Delta H_m = -5212.545 \ 696 \text{ J mol}^{-1}$$

$$\Delta H = n\Delta H_m$$

$$\Delta H = (0.1 \text{ mol})(-5212.545 \ 696 \text{ J mol}^{-1})$$

$$\Delta H = -521.2 \ 545 \ 696 \text{ J}$$

$$\boxed{\Delta H = -521.15 \text{ J}}$$

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**2.46.** A gas behaves ideally and its  $C_V$  is given by

$$C_V/\text{J K}^{-1} \text{ mol}^{-1} = 21.52 + 8.2 \times 10^{-3} T/\text{K}$$

**a.** What is  $C_{P,m}$  as a function of  $T$ ?

**b.** A sample of this gas is initially at  $T_1 = 300 \text{ K}$ ,  $P_1 = 10 \text{ bar}$ , and  $V_1 = 1 \text{ dm}^3$ . It is allowed to expand until  $P_2 = 1 \text{ bar}$  and  $V_2 = 10 \text{ dm}^3$ . What are  $\Delta U$  and  $\Delta H$  for this process? Could the process be carried out adiabatically?

**Solution:**

Given: Ideal Gas:  $C_V = 21.52 + 8.2 \times 10^{-3} T / \text{K}$ ,  $T_1 = 300 \text{ K}$ ,  $P_1 = 10 \text{ bar}$ ,  $V_1 = 1 \text{ dm}^3$

$$P_2 = 1 \text{ bar}, V_2 = 10 \text{ dm}^3$$

Required:  $C_{P,m}$ ,  $\Delta U$ ,  $\Delta H$

**a.** Just as in Problem 2.45, we can use Eq. 2.119 in order to determine  $C_{P,m}$  given the value (or the equation for the value) of  $C_{V,m}$ .

$$C_{P,m} - C_{V,m} = R$$

$$C_{P,m} - C_{V,m} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{P,m} - (21.52 + 8.2 \times 10^{-3} \{T / \text{K}\}) = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{C_{P,m} = 29.8345 \text{ J K}^{-1} \text{ mol}^{-1} + 8.2 \times 10^{-3} \{T / \text{K}\}}$$

Recall that both the increase in internal energy and in enthalpy are given by Eqs. 2.95 and 2.96;

$$\Delta U_m = C_{V,m} (T_f - T_i)$$

$$\Delta H_m = C_{P,m} (T_f - T_i)$$

However, we first need to determine the final temperature by using Eq. 2.91 and the information given above.

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i}$$

$$T_f = \frac{T_i P_f V_f}{P_i V_i}$$

$$T_f = \frac{(300 \text{ K})(1 \text{ bar})(10 \text{ dm}^3)}{(10 \text{ bar})(1 \text{ dm}^3)}$$

$$T_f = 300 \text{ K}$$

**b.** Since there is no change in temperature, then we find that:

$$\Delta U_m = C_{V,m} (T_f - T_i)$$

$$\Delta U_m = C_{V,m} (0)$$

$$\Delta U_m = 0$$

$$\text{therefore, } \boxed{\Delta U = 0}$$

$$\Delta H_m = C_{P,m} (T_f - T_i)$$

$$\Delta H_m = C_{P,m} (0)$$

$$\Delta H_m = 0$$

$$\text{therefore, } \boxed{\Delta H = 0}$$

Recall that adiabatic processes take place in vessels whose walls are perfectly insulated. This means that no heat can be transferred to or from the control volume. We indeed could perform this process under adiabatic conditions by allowing free expansion which means that  $w = q = 0$ .

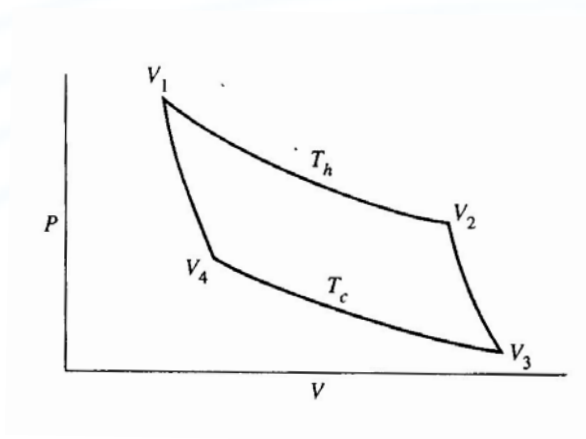
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**2.47.** Prove that for an ideal gas two reversible adiabatic curves on a  $P$ - $V$  diagram cannot intersect.

**Solution:**

The diagram given below displays two adiabatic pathways for an ideal gas. These adiabatic pathways are intersected by two isotherms corresponding to the temperatures  $T_h$  and  $T_c$ . Take careful note to compare this diagram with Figure 3.2a.



To show mathematically that for an ideal gas, two reversible adiabatic curves on a  $P$ - $V$  diagram cannot intersect, we will use Eq. 2.90 which gives,

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma-1}$$

$$\frac{T_h}{T_c} = \left( \frac{V_4}{V_1} \right)^{\gamma} \text{ as well as } \frac{T_h}{T_c} = \left( \frac{V_3}{V_2} \right)^{\gamma}$$

From this we can deduce that:

$$\left(\frac{V_4}{V_1}\right)^\gamma = \left(\frac{V_3}{V_2}\right)^\gamma$$

$$\left(\frac{V_4}{V_1}\right) = \left(\frac{V_3}{V_2}\right) \text{ or } \left(\frac{V_2}{V_1}\right) = \left(\frac{V_3}{V_4}\right)$$

Thus, if any isotherm is drawn to intersect the two adiabatic pathways, the ratio of the volume at the intersection points is always the same. This means that it is not possible for the adiabatic pathways to intersect.

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**2.48.** An ideal gas is defined as one that obeys the relationship  $PV = nRT$ . We showed in Section 2.7 that for such gases

$$(\partial U/\partial V)_T = 0 \text{ and } (\partial H/\partial P)_T = 0$$

Prove that for an ideal gas  $C_V$  and  $C_P$  are independent of volume and pressure.

**Solution:**

Recall that  $C_V$  is defined by Eq. 2.45 which states that,

$$C_V = \left( \frac{\partial \Delta U}{\partial T} \right)_V$$

From this, we can say that,

$$\left( \frac{\partial C_V}{\partial V} \right)_T = \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T$$

Since we are given that  $(\partial U/\partial V)_T = 0$  for an ideal gas, then it is possible to see that from the above,  $(\partial C_V/\partial V)_T$  is also equal to zero. This means that  $C_V$  is independent of both volume and pressure as only temperature is being held constant. Similarly, for  $C_P$  we have:

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

$$\left( \frac{\partial C_P}{\partial P} \right)_T = \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial T} \right)_P = \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial P} \right)_T$$

Since we are given that  $(\partial H/\partial P)_T = 0$  for an Ideal Gas, thus it is possible to see that from the above,  $(\partial C_P/\partial P)_T$  is also equal to zero. This means that  $C_P$  is independent of both volume and pressure as only temperature is being held constant.

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**2.49.** One mole of an ideal gas underwent a reversible isothermal expansion until its volume was doubled. If the gas performed 1 kJ of work, what was its temperature?

**Solution:**

Given: Ideal Gas: 1 mole, reversible isothermal expansion,  $w = 1\text{kJ}$

Required:  $T$

Remember that a reversible isothermal expansion or compression of an ideal gas occurs along an isotherm (which means at constant temperature!). Such a process is illustrated in Figure 2.6c. We have already seen the equations corresponding to this type of process. We have also gone through the derivation for Eq. 2.72 which gives the work done ON the system in a reversible compression or expansion;

$$w_{\text{rev}} = RT \ln \left( \frac{V_{m,1}}{V_{m,2}} \right)$$

However, since we are being asked for the work *done by* the gas, we must take the negative of this value (same magnitude, just opposite sign).

$$-w_{\text{rev}} = RT \ln \left( \frac{V_{m,2}}{V_{m,1}} \right) \quad (\text{Eq. 2.74})$$

In this particular case, we are given that,  $n = 1 \text{ mol}$ ,  $-w = 1000 \text{ J}$  and  $\frac{V_{m,2}}{V_{m,1}} = 2$ . Thus,

$$1000 \text{ J} = (1\text{mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times T \times \ln(2)$$

$$T = \frac{1000 \cancel{\text{J}} \cancel{\text{mol}^{-1}}}{8.3145 \cancel{\text{J}} \text{ K}^{-1} \cancel{\text{mol}^{-1}} \times \ln(2)}$$

$$T = 173.5 \text{ K}$$

$$\boxed{T = 173.5 \text{ K}}$$

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**2.50.** A gas that behaves ideally was allowed to expand reversibly and adiabatically to twice its volume. Its initial temperature was 25.00 °C, and  $C_{V,m} = (5/2)R$ . Calculate  $\Delta U_m$  and  $\Delta H_m$  for the expansion process.

**Solution:**

Given: Ideal Gas:  $T_i = 25.00\text{ °C}$ ,  $C_{V,m} = \frac{5}{2}R$

Required:  $\Delta U_m$ ,  $\Delta H_m$

Since we already know that  $C_{V,m} = (5/2)R$  we can determine  $C_{P,m}$  by rearranging Eq. 2.119,

$$C_{P,m} = C_{V,m} + R$$

$$C_{P,m} = \frac{5}{2}R + R$$

$$C_{P,m} = \frac{7}{2}R$$

We can now determine the ratio of the two heat capacities,  $\gamma$ ;

$$\gamma = \frac{C_{P,m}}{C_{V,m}}$$

$$\gamma = \frac{\frac{7}{2}}{\frac{5}{2}} = \frac{7}{\cancel{2}} \times \frac{\cancel{2}}{5} = \frac{7}{5}$$

We have been given the initial temperature as well as the ratio between the final and initial volumes so that we can use Eq. 2.90 in order to solve for the final temperature.

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma-1}$$

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{\gamma-1}$$

$$T_f = (298.15 \text{ K}) \left( \frac{1}{2} \right)^{\frac{7}{5}-1}$$

$$T_f = (298.15 \text{ K}) \left( \frac{1}{2} \right)^{\frac{2}{5}}$$

$$T_f = 225.955 \ 447 \ 2 \text{ K}$$

We can again (as in the last few previous problems) use Eq. 2.95 and Eq. 2.96 in order to solve for  $\Delta U_m$  and  $\Delta H_m$ .

$$\Delta U_m = C_{V,m} \Delta T$$

$$\Delta U_m = \frac{5}{2} (8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1}) (225.9 \ 554 \ 472 - 298.15) \cancel{\text{K}}$$

$$\Delta U_m = -1500.654 \ 024 \text{ J mol}^{-1}$$

$$\Delta U_m = -1500 \text{ J mol}^{-1}$$

$$\boxed{\Delta U_m = -1.5 \text{ kJ mol}^{-1}}$$

$$\Delta H_m = C_{P,m} \Delta T$$

$$\Delta H_m = \frac{7}{2} (8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1}) (225.9 \ 554 \ 472 - 298.15) \cancel{\text{K}}$$

$$\Delta H_m = -2100.915 \ 632 \text{ J mol}^{-1}$$

$$\Delta H_m = -2100 \text{ J mol}^{-1}$$

$$\boxed{\Delta H_m = -2.1 \text{ kJ mol}^{-1}}$$

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- 2.51.** With  $C_{V,m} = (3/2)R$ , 1 mol of an ideal monatomic gas undergoes a reversible process in which the volume is doubled and in which 1 kJ of heat is absorbed by the gas. The initial pressure is 1 bar and the initial temperature is 300 K. The enthalpy change is 1.50 kJ.
- Calculate the final pressure and temperature.
  - Calculate  $\Delta U$  and  $w$  for the process.

**Solution:**

Given: Ideal Gas:  $C_{V,m} = \frac{3}{2}R$ ,  $n = 1$  mol,  $heat = 1$  kJ,  $P_i = 1$  bar,  $T_i = 300$  K,  $\Delta H = 1.50$  kJ

Required:  $P_f$ ,  $T_f$ ,  $\Delta U_m$ ,  $w$

- Since we have already been given the enthalpy change and the value for the molar heat capacity at constant volume, we can find the value for the molar heat capacity at constant pressure.

$$C_{P,m} - C_{V,m} = R$$

$$C_{P,m} = C_{V,m} + R$$

$$C_{P,m} = \frac{3}{2}R + R$$

$$C_{P,m} = \frac{5}{2}R$$

Since we know that  $\Delta H = C_p \Delta T$ , we can get the expression;

$$1500 \text{ J mol}^{-1} = \left(20.79 \text{ J } \cancel{\text{K}}^{\circ} \text{ mol}^{-1}\right) (T_f - 300) \cancel{\text{K}}$$

Solving first for the final temperature we get,

$$(T_f - 300) \text{ K} = \frac{(1500 \text{ J mol}^{-1})}{(20.79 \text{ J K}^{-1} \text{ mol}^{-1})}$$

$$T_f = \frac{(1500 \text{ J mol}^{-1})}{(20.79 \text{ J K}^{-1} \text{ mol}^{-1})} + 300 \text{ K}$$

$$T_f = 372.150 \text{ 072 2 K}$$

$$\boxed{T_f = 372.15 \text{ K}}$$

The final pressure can be found using a rearrangement of Eq. 2.91,

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i}$$

$$\frac{P_f}{P_i} = \frac{T_f}{T_i} \times \frac{V_i}{V_f}$$

$$\frac{P_f}{P_i} = \frac{372.150 \text{ 072 2 K}}{300 \text{ K}} \times \frac{1}{2}$$

$$\frac{P_f}{P_i} = 0.620 \text{ 250 12}$$

$$P_f = P_i (0.620 \text{ 250 12})$$

$$P_f = (1 \text{ bar})(0.620 \text{ 250 12})$$

$$P_f = 0.620 \text{ 250 12 bar}$$

$$\boxed{P_f = 0.62 \text{ bar}}$$

**b.** It follows that the change in internal energy would be,

$$\Delta U_m = C_{V,m} \Delta T$$

$$\Delta U_m = \frac{3}{2} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (372.150\,072\,2 - 300) \text{ K}$$

$$\Delta U_m = 899.837\,663 \text{ J mol}^{-1}$$

$$\boxed{\Delta U_m = 900 \text{ J mol}^{-1}}$$

Since the heat is absorbed BY the gas, work is defined as  $w = \Delta U - q$ , which, when making the appropriate substitutions, will yield:

$$w = 899.837\,663 \text{ J mol}^{-1} - 1000 \text{ J mol}^{-1}$$

$$w = -100.162\,337 \text{ J mol}^{-1}$$

$$\boxed{w = -100 \text{ J mol}^{-1}}$$

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**2.52.** Prove that:

$$C_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$$

**Solution:**

Remember again that  $C_V$  is defined as (according to Eq. 2.25):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Flip to Appendix C or try to remember Euler's Chain Rule from calculus. We will see that, if a function depends on two or more variables, the partial derivative relates to the dependence of say,  $z$  on one variable with all other variables held constant. This would be if we were working with the differential,

$$\left(\frac{\partial z}{\partial x}\right)_y \text{ which expresses the dependence of } z \text{ on } x \text{ when } y \text{ is held constant.}$$

If  $z$  is a function of  $x$  and  $y$ , Eq. C.6 (from Appendix C) will apply and we can then hold  $z$  constant and divide by  $dx$  to get the following:

$$\begin{aligned} dz &= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \\ 0 &= \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \end{aligned}$$

We must then apply Eq. C.9 which will yield,

$$\begin{aligned} \left(\frac{\partial z}{\partial x}\right)_y &= \frac{1}{(\partial x / \partial z)_y} \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -1 \\ \text{or } \left(\frac{\partial z}{\partial x}\right)_y &= -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \end{aligned}$$

The last expression above is called *Euler's Chain Rule*. Let us now apply this logic to the current system.

We can equate  $\left(\frac{\partial z}{\partial x}\right)_y$  with  $\left(\frac{\partial U}{\partial T}\right)_V$  which means that we can also equate  $\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$  with  $\left(\frac{\partial U}{\partial T}\right)_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$ . This would then mean that,

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U}$$

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**2.53.** Prove that for an ideal gas the rate of change of the pressure  $dP/dt$  is related to the rates of change of the volume and temperature by

$$\frac{1}{P} \frac{dP}{dt} = -\frac{1}{V} \frac{dV}{dt} + \frac{1}{T} \frac{dT}{dt}$$

**Solution:**

Given: Ideal Gas

Required:  $\frac{dP}{dt}$  as it relates to  $\frac{dV}{dt}$  and  $\frac{dT}{dt}$

From Appendix C, we are given the general relationship between pressure, volume and temperature by again making use of Eq. C.6 and then applying the partial derivative  $\left(\frac{\partial z}{\partial x}\right)_y$ . Then the total derivative becomes,

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

From the Ideal Gas Law,  $PV = nRT$  in the form  $P = \frac{nRT}{V}$  we can find the two required partial derivatives that appear in the differential equation.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} = \frac{P}{T}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} = -\frac{P}{V}$$

Substitution gives,

$$dP = \frac{P}{T} dT - \frac{P}{V} dV$$

and upon rearrangement and differentiation with respect to  $t$ , gives



$$\boxed{\frac{1}{P} \frac{dP}{dt} = \frac{1}{T} \frac{dT}{dt} - \frac{1}{V} \frac{dV}{dt}}$$

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**2.54.** Initially 5 mol of nitrogen are at a temperature of 25 °C and a pressure of 10 bar. The gas may be assumed to be ideal;  $C_{V,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$  and is independent of temperature. Suppose that the pressure is *suddenly* dropped to 1 bar; calculate the final temperature,  $\Delta U$ , and  $\Delta H$ .

**Solution:**

Given: Nitrogen:  $n_{\text{nitrogen}} = 5 \text{ mol}$ ,  $T_i = 25^\circ\text{C}$ ,  $P_i = 10 \text{ bar}$ ,  $C_{V,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $P_f = 1 \text{ bar}$

Required:  $T_f$ ,  $\Delta U$ ,  $\Delta H$

From Eq. 2.95 written for one mole,

$$\Delta U_m = C_{V,m} (T_2 - T_1)$$

For  $n$  moles,

$$\Delta U_m = n C_{V,m} \Delta T$$

Taking the differentials we have,

$$dU = n C_{V,m} dT$$

From Eq. 2.74,

$\Delta U_m = q_{\text{rev}} + w_{\text{rev}}$  we may also write,

$$dU = dq + dw \text{ where } dw = -PdV = -\frac{nRT}{V} dV$$

Since  $dq=0$

$$n C_{V,m} dT = -\frac{nRT}{V} dV$$

Rearranging and integrating yields

$$C_{V,m} \ln \frac{T_f}{T_i} = -R \ln \frac{V_f}{V_i}$$

$$\ln T_f - \ln T_i = \frac{-R}{C_{V,m}} (\ln V_f - \ln V_i)$$

$$\ln T_f - \ln T_i = \frac{-R}{C_{V,m}} \left( \ln \frac{RT_f}{P_f} - \ln \frac{RT_i}{P_i} \right)$$

$$\ln T_f - \ln T_i = \frac{-R}{C_{V,m}} \left( \ln \frac{R}{P_f} + \ln T_f - \ln \frac{RT_i}{P_i} \right)$$

Rearranging yields,

$$\ln T_f = \frac{-\frac{R}{C_v} \left( \ln \frac{R}{P_f} - \ln \frac{RT_i}{P_i} \right) + \ln T_i}{1 + \frac{R}{C_v}}$$

$$\ln T_f = \frac{-\frac{8.3145}{20.8} \left( \ln \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{100000 \text{ Pa}} - \ln \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{1000000 \text{ Pa}} \right) + \ln(298.15 \text{ K})}{1 + \frac{8.3145}{20.8}}$$

$$\ln T_f = 5.040\,025\,96$$

$$T_f = \exp(5.040\,025\,96)$$

$$T_f = 154.474\,025\,2 \text{ K}$$

$$\boxed{T_f = 155 \text{ K}}$$

Solving for the energy we obtain,

$$\Delta U = nC_v\Delta T$$

$$\Delta U = 5 \text{ mol} \times 20.8 \text{ J K}^{-1}\text{mol}^{-1} \times (154.474 \text{ 025 2 K} - 298.15 \text{ K})$$

$$\Delta U = -14 \text{ 942.301 38 J}$$

$$\boxed{\Delta U = -14 \text{ 942 J}}$$

$$\Delta H = nC_p\Delta T$$

$$\Delta H = 5 \text{ mol} \times (20.8 + 8.3145) \text{ J K}^{-1}\text{mol}^{-1} \times (154.474 \text{ 025 2 K} - 298.15 \text{ K})$$

$$\Delta H = -20 \text{ 915.270 87 J}$$

$$\boxed{\Delta H = -20 \text{ 915 J}}$$

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**2.55.** A chemical reaction occurs at 300 K in a gas mixture that behaves ideally, and the total amount of gas increases by 0.27 mol. If  $\Delta U = 9.4$  kJ, what is  $\Delta H$ ?

**Solution:**

Given: Ideal Gas:  $T_i = 300$  K,  $\Delta n = 0.27$  mol,  $\Delta U = 9.4$  kJ

Required:  $\Delta H$

We know that the system initially contains  $n$  moles. When the reaction has occurred an extra 0.27 moles has been formed. So the extra 0.27 moles has caused a  $\Delta PV$  change since the temperature remains constant. The relationship is,

$$\Delta(PV) = \Delta nRT$$

$$\Delta(PV) = (0.27 \text{ mol})RT$$

Since in Eq. 2.41 we have

$$\Delta H = \Delta U + \Delta(PV),$$

substitution of the value of  $0.27RT$  for  $\Delta PV$  and the given value of  $\Delta U$  gives,

$$\Delta(PV) = (0.27 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})$$

$$\Delta(PV) = 673.4745 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = 9400 \text{ J} + 673.4745 \text{ J}$$

$$\Delta H = 10\,073.4745 \text{ J}$$

$$\boxed{\Delta H = 10.07 \text{ kJ}}$$

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**2.56.** Suppose that 1.00 mol of an ideal monatomic gas ( $C_V = (3/2)R$ ) at 1 bar is adiabatically and reversibly compressed starting at 25.0 °C from 0.1000 m<sup>3</sup> to 0.0100 m<sup>3</sup>. Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

**Solution:**

Given: Ideal Monatomic Gas:  $C_V = \frac{3}{2}R$ ,  $P = 1$  bar,  $T_i = 25$  °C,  $V_i = 0.1000$  m<sup>3</sup>,  $V_f = 0.0100$  m<sup>3</sup>

Required:  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$

In this problem, we are considering an ideal gas contained in a vessel whose walls are perfectly insulating (no heat exchange), this is called an adiabatic process. Since work is performed ON the gas in order to compress it and no heat can leave the system, the final temperature must be higher than the initial one.

By now we have seen Eq. 2.95 and Eq. 2.96 many times and we also know that *both*  $U$  and  $H$  remain unchanged as we move along an isothermal pathway. Since we know that;

$$\Delta U = C_V \Delta T \text{ and } \Delta H = C_P \Delta T$$

And from Eq. 2.41  $\{\Delta H = \Delta U + \Delta(PV)\}$  as well as  $\{\Delta U = q + w\}$  from Chapter 1, we can formulate a pertinent expression for the work *done on* the gas during the compression. It is extremely important to note that since we are working under adiabatic conditions, this implies that  $q = 0$ . This helps to simplify the expression for work.

The fact is that the gas is undergoing a compression so  $P$ - $V$  work is being done, thus

$$w = P\Delta V = P(V_f - V_i)$$

$$w = (1 \text{ bar})(0.0100 \text{ m}^3 - 0.1000 \text{ m}^3)$$

$$w = (1 \text{ bar})(-0.09 \text{ m}^3)$$

Now we should change the units in order to express this in joules. Therefore, we must make all the appropriate substitutions.

1 bar =  $10^5$  Pa, therefore,

$$w = (10^5 \text{ Pa}) \times (-0.09 \text{ m}^3)$$

$$w = -9000 \text{ Pa m}^3$$

since  $1 \text{ Pa} = 1 \frac{\text{kg}}{\text{m s}^2}$  and  $1 \text{ J} = \frac{\text{kg m}^2}{\text{s}^2}$ ,  $1 \text{ J} = \text{m}^3 \text{ Pa}$

$$\boxed{w = -9000 \text{ J}}$$

Now we can find the final temperature using the Ideal Gas Law. This will enable us to determine the change in enthalpy and internal energy.

$$PV_f = nRT_f$$

$$T_f = \frac{PV_f}{nR}$$

$$T_f = \frac{(10^5 \text{ Pa})(0.0100 \text{ m}^3)}{(1 \text{ mol})(0.083145 \text{ J K}^{-1} \text{ mol}^{-1})}$$

$$T_f = 120.264 \text{ 582 1 K}$$

for  $n$  moles,

$$\Delta U_m = nC_{V,m}\Delta T$$

$$\Delta U_m = (1 \text{ mol})\left(\frac{3}{2} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)(120.264 \text{ 582 1} - 298.15) \text{ K}$$

$$\Delta U_m = -2 \text{ 218.542 461 J}$$

$$\boxed{\Delta U_m = -2.22 \text{ kJ}}$$

We can solve for the enthalpy change by using Eq. 2.96 which yields,

$$C_{P,m} - C_{V,m} = R$$

$$C_{P,m} = C_{V,m} + R$$

$$C_{P,m} = \frac{3}{2}R + R = \frac{5}{2}R$$

for  $n$  moles,

$$\Delta H_m = nC_{P,m}\Delta T$$

$$\Delta H_m = (1 \text{ mol}) \left( \frac{5}{2} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) (120.2645821 - 298.15) \text{ K}$$

$$\Delta H_m = -3697.570768 \text{ J}$$

$$\boxed{\Delta H_m = -3.70 \text{ kJ}}$$

Lastly, we will make use of the fact that  $\{\Delta U = q + w\}$  in order to solve for the amount of heat generated by the compression.

$$\Delta U = q + w$$

$$q = \Delta U - w$$

$$q = [-2218.542461 - (-9000)] \text{ J}$$

$$q = 6781.457539 \text{ J}$$

$$\boxed{q = 6.78 \text{ kJ}}$$

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**2.57.** Suppose that an ideal gas undergoes an irreversible isobaric adiabatic process. Derive expressions for  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  and the final temperature of the gas undergoing the process.

**Solution:**

Given: Ideal Gas: irreversible isobaric process

Required: expressions for  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $T_f$

It is important to note the conditions of this problem! The term isobaric means that the process is executed under constant pressure. We also remember that adiabatic means that there is no heat exchange between the material inside the vessel and the surroundings (the vessel walls are impermeable). In addition, we need to account for the fact that this process is an *irreversible* one. Mathematically, this all generates the following;

Isobaric  $P_1 = P_2 = P$

Adiabatic  $q = 0$  and  $w = P\Delta V$

Therefore,

$$\Delta U = \cancel{q} + w$$

$$\Delta U = w$$

$$\Delta U = P\Delta V$$

$$PV_f = nRT_f$$

$$T_f = \frac{PV_f}{nR}$$

As for the enthalpy change, there are a couple of different ways that it can be found. We will use the fact that for an ideal monatomic gas,  $C_P = 5/2R$ :

$$\Delta H_m = C_{P,m} \Delta T$$

$$\Delta H = \frac{5}{2} R (T_f - T_i)$$

$$\Delta H = \frac{5}{2} R \left( \frac{PV_f}{nR} - T_i \right)$$

Or, we can use Eq. 2.41 which gives,  $\Delta H = \Delta U + \Delta(PV)$  and if the correct values are used throughout the exercise, this should still be valid for an ideal monatomic gas.

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**2.58.** Exactly one mole of an ideal monatomic gas at 25.0 °C is cooled and allowed to expand from 1.00 dm<sup>3</sup> to 10.00 dm<sup>3</sup> against an external pressure of 1.00 bar. Calculate the final temperature, and  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

**Solution:**

Given: Ideal Monatomic Gas:  $T_i = 25\text{ °C}$ ,  $V_i = 1.00\text{ dm}^3$ ,  $V_f = 10.00\text{ dm}^3$ ,  $P_{ext} = 1.00\text{ bar}$

Required:  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $T_f$

Given the pressure as well as the final and initial volumes, we can determine the final temperature by using the same method as we did in previous problems.

$$P_{ext} V_f = nRT_f$$

$$T_f = \frac{P_{ext} V_f}{nR}$$

$$T_f = \frac{(1.00 \cancel{\text{ bar}})(10.00 \cancel{\text{ dm}^3})}{(1.00 \cancel{\text{ mol}})(0.08315 \cancel{\text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}})}$$

$$T_f = 120.2645821\text{ K}$$

$$\boxed{T_f = 120.3\text{ K}}$$

In this process, it is the gas that is doing the work while expanding against a constant external pressure. Knowing that the work done ON the system in a reversible compression is:

$$w = -\int_{V_{m,1}}^{V_{m,2}} P dV$$

We can determine the work done *by* the gas against the external pressure by doing the integration and making a substitution.

$$PV_m = nRT$$

$$P = \frac{nRT}{V_m}$$

$$w = - \int_{V_{m,1}}^{V_{m,2}} \frac{nRT}{V_m} dV$$

$$w = -nRT \ln V_m \Big|_{V_{m,1}}^{V_{m,2}}$$

$$w = -nRT \ln \left( \frac{V_{m,2}}{V_{m,1}} \right)$$

$$w = nRT \ln \left( \frac{V_{m,1}}{V_{m,2}} \right)$$

$$w = (1.00 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (120.264 \text{ 582 1 K}) \ln \left( \frac{1.00}{10.00} \right)$$

$$w = -2 \text{ 302.446 633 J}$$

$$\boxed{w = -2.30 \text{ kJ}}$$

We will solve for  $q$ ,  $\Delta U$  and  $\Delta H$  in the same way as we have been doing for the past few problems.

$$\Delta H = nC_p\Delta T$$

ideal monatomic gas;

$$\Delta H = n \frac{5}{2} R \Delta T$$

$$\Delta H = (1.00 \text{ mol}) \left( \frac{5}{2} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) (120.264 \text{ 582 1} - 298.15) \text{ K}$$

$$\Delta H = -3 \text{ 697.570 768 J}$$

$$\boxed{\Delta H = -3.70 \text{ kJ}}$$

$$\Delta U = nC_v\Delta T$$

ideal monatomic gas;

$$\Delta U = n\frac{3}{2}R\Delta T$$

$$\Delta U = (1.00 \text{ mol})\left(\frac{3}{2} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)(120.264 \text{ 582 1} - 298.15) \text{ K}$$

$$\Delta U = -2 \text{ 218.542 461 J}$$

$$\boxed{\Delta U = -2.22 \text{ kJ}}$$

Finally, we can solve for the amount of heat generated during this reaction.

$$\Delta U = q + w$$

$$q = \Delta U - w$$

$$q = [(-2 \text{ 218.542 461}) - (-2 \text{ 302.446 633})] \text{ J}$$

$$q = 83.90 \text{ 417 231 J}$$

$$\boxed{q = 8.39 \times 10^{-2} \text{ kJ}}$$

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**2.59.** A balloon 15 m in diameter is inflated with helium at 20 °C.

- a. What is the mass of helium in the balloon, assuming the gas to be ideal?
- b. How much work is done by the balloon during the process of inflation against an external pressure of 1 atm (101.315 kPa), from an initial volume of zero to the final volume?

**Solution:**

Given: Helium:  $d_{\text{balloon}} = 15 \text{ m}$ ,  $T_i = 20 \text{ °C}$ ,  $P_{\text{ext}} = 1.00 \text{ atm}$ ,  $V_i = 0 \text{ dm}^3$

Required:  $m_{\text{balloon}}$ ,  $w(\text{by balloon})$

- a. Assuming the balloon is a perfect sphere,

$$V_{\text{sphere}} = \frac{4}{3} \pi r^3$$

Remembering that the diameter is twice the radius, we can write;

$$V_{\text{balloon}} = \frac{4}{3} \pi \left( \frac{d}{2} \right)^3$$

$$V_{\text{balloon}} = \frac{4}{3} \pi \left( \frac{15}{2} \right)^3$$

$$V_{\text{balloon}} = \frac{4}{3} \pi (7.5)^3$$

$$V_{\text{balloon}} = 1\,767.145\,868 \text{ m}^3$$

We are now able to determine the amount of helium present in the inflated balloon (the number of moles) by using the Ideal Gas Law.

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$1 \text{ atm} = 1.013\,25 \times 10^5 \text{ Pa}$$

$$n = \frac{(1.013\,25 \times 10^5 \text{ Pa})(1\,767.145\,868 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})}$$

$$n = 73\,462.038\,55 \text{ mol}$$

From the periodic table of the elements, we can approximate that the molar mass of helium is  $4.026 \text{ g mol}^{-1}$ . We now have enough information to find the mass of the balloon.

$$m_{\text{balloon}} = n \times M$$

$$m_{\text{balloon}} = (73\,462.03\,855 \text{ mol})(4.026 \text{ g mol}^{-1})$$

$$m_{\text{balloon}} = 295\,758.167\,2 \text{ g}$$

$$\boxed{m_{\text{balloon}} = 295.8 \text{ kg}}$$

**b.** The work *done by* the balloon in question during an expansion against a constant external pressure is given by Eq. 2.12:

$$w = -P \int_{V_1}^{V_2} dV$$

$$w = -P(V_2 - V_1)$$

$$w = -P\Delta V$$

Remember that when the system is *doing work*, we must switch the signs to get;

$$w = -P \int_{V_i}^{V_f} dV$$

$$w = -P(V_f - V_i)$$

$$w = -P\Delta V$$

$$-w = P\Delta V$$

$$\text{note that } V_i = 0$$

$$-w = (1.01\,325 \times 10^5 \text{ Pa})(1\,767.145\,868 \text{ m}^3)$$

$$-w = 179\,056\,055.1 \text{ J}$$

$$\boxed{-w = 1.79 \times 10^5 \text{ kJ}}$$

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- 2.60.** a. Calculate the work done when 1 mol of an ideal gas at 2 bar pressure and 300 K is expanded isothermally to a volume of 1.5 L, with the external pressure held constant at 1.5 bar.  
 b. Suppose instead that the gas is expanded isothermally and *reversibly* to the same final volume; calculate the work done.

**Solution:**

Given: Ideal Gas:  $n = 1$  mol,  $P_i = 2$  bar,  $T_i = 300$  K,  $V_f = 1.5$  L,  $P_{\text{ext}} = 1.5$  bar

Required:  $w$  done in both cases

- a. Under isothermal conditions, we already know that the temperature is being held constant. We also need to consider that this expansion is occurring against an external pressure just like in Problem 2.59. With the information that we have, we should start by trying to find the initial volume for the gas using the Ideal Gas Law.

$$PV = nRT$$

$$V_i = \frac{nRT_i}{P_i}$$

$$V_i = \frac{(1.0 \text{ mol})(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{2 \text{ bar}}$$

$$V_i = 12.4725 \text{ dm}^3$$

By combining the gas laws for both the initial and final reaction conditions, we will be able to determine the final volume in cubic decimeters. Take note that the final pressure is equal to the constant external pressure value.

$$V_f = \frac{P_i V_i}{P_f}$$

$$V_f = \frac{(2.0 \text{ bar})(12.4725 \text{ dm}^3)}{(1.5 \text{ bar})}$$

$$V_f = 16.63 \text{ dm}^3$$

The system exerts pressure-volume work, so we can say that:

$$w = -P_{\text{ext}} \Delta V$$

$$w = (-1.5 \text{ bar})(16.63 - 12.4725) \text{ dm}^3$$

$$w = -6.236 \text{ 25 bar dm}^3$$

$$1 \text{ bar} = 10^5 \text{ Pa}, 1 \text{ atm} = 1.013 \text{ 25} \times 10^5 \text{ Pa}$$

$$w = (-6.236 \text{ 25 } \cancel{\text{bar}} \text{ dm}^3) \times (10^5 \cancel{\text{Pa}} \cancel{\text{bar}^{-1}}) \times \left( \frac{1 \text{ atm}}{1.013 \text{ 25} \times 10^5 \cancel{\text{Pa}}} \right)$$

$$w = -6.154 \text{ 700 222 atm dm}^3$$

$$1 \text{ atm dm}^3 = 101.325 \text{ J therefore,}$$

$$w = (-6.154 \text{ 700 222 } \cancel{\text{atm dm}^3}) \times \frac{101.325 \text{ J}}{1 \cancel{\text{atm dm}^3}}$$

$$w = -623.625 \text{ J}$$

$$\boxed{w = -624 \text{ J}}$$

Remember that when the work provides a negative number, it means that the gas itself is the component doing the work. This is obvious when we consider the fact that the process is an expansion against constant pressure.

- b.** Now we will imagine that the gas is being expanded isothermally and *reversibly* to the same final volume. This means that the process is occurring at constant temperature. This process is called reversible isothermal expansion. Note that since there is no change in temperature throughout the reaction, the changes in internal energy and enthalpy will also be equal to zero due to their dependence on temperature change.

The work *done on* the system in a reversible *compression* is given by Eq. 2.70:

$$w_{\text{rev}} = -\int_{V_{m,1}}^{V_{m,2}} P dV$$

$$P = \frac{nRT}{V}$$

$$w_{\text{rev}} = -nRT \ln V \Big|_{V_{m,1}}^{V_{m,2}}$$

$$w_{\text{rev}} = -nRT \ln \left( \frac{V_{m,2}}{V_{m,1}} \right)$$

$$w_{\text{rev}} = (-1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln \left( \frac{16.63}{12.4725} \right)$$

$$w_{\text{rev}} = -717.579 \text{ J}$$

$$\boxed{w_{\text{rev}} = -718 \text{ J}}$$

As we have just observed, the gas is actually doing *more* work in the reversible isothermal pathway. The difference in work done is 94 J.

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- 2.61.** The heat capacity difference can be determined experimentally in terms of the two variables  $\alpha$  and  $\beta$  in the equation for an ideal gas. Determine the value of  $C_P$  and  $C_V$  for an ideal gas in the equation  $C_P - C_V = TV\alpha^2/\beta$  where

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \text{ and } \beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T.$$

**Solution:**

Given: see above

Required:  $C_P$  and  $C_V$

For an Ideal Gas, we know that  $PV = nRT$ . This equation can be rearranged to solve for any missing variable. From the two equations given, we see that we must differentiate volume as our known with respect to  $P$  and also with respect to  $T$ , holding the other variables constant. We rearrange the expression so that the volume can be isolated.

$$V = \frac{RT}{P} \text{ this expression is for one mole of substance}$$

We now can evaluate the two given differentials in the problem for one mole of gas.

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\left( \frac{\partial V}{\partial P} \right)_T = \left( \frac{-1}{P^2} \right) RT$$

$$\left( \frac{\partial V}{\partial P} \right)_T = -\left( \frac{RT}{P^2} \right)$$

$$\text{Now substitute these values into } \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \text{ and } \beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T.$$

Substituting these values for  $\alpha$  and  $\beta$  into the given equation  $C_P - C_V = TV \frac{\alpha^2}{\beta}$ , we obtain,

$$C_p - C_v = TV \frac{\left(\frac{1}{V}\right)^2 \left(\frac{R}{P}\right)^2}{\left(-\frac{1}{V}\right) \left(\frac{-RT}{P^2}\right)}$$

$$C_p - C_v = TV \frac{\left(\frac{R^2}{V^2 P^2}\right)}{\left(\frac{RT}{VP^2}\right)}$$

Now we simplify to obtain,

$$C_p - C_v = (\cancel{T} \cancel{V}) \left( \frac{\cancel{R}^2}{\cancel{V}^2 \cancel{P}^2} \right) \left( \frac{\cancel{V} \cancel{P}^2}{\cancel{R} \cancel{T}} \right)$$

$$C_p - C_v = R$$

$$\boxed{C_p - C_v = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**2.62.** For an ideal gas,  $PV_m = RT$  and therefore  $(dT/dP)_V = V_m/R$ . Derive the corresponding relationship for a van der Waals gas.

**Solution:**

Given: Ideal Gas:  $PV = RT$ ,  $\left(\frac{dT}{dP}\right)_V = \frac{V_m}{R}$

Required: same relationship for a van der Waals gas

This last section of problems for Chapter 2 concern *Real Gases*. It is important that you are familiar with all of the material regarding Real Gases from Chapter 1. We were given that for a single mole of a *real* gas, the Van der Waals Equation is written;

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (\text{Eq. 2.100})$$

We came to this expression by starting with the Ideal Gas Law then making small adjustments to compensate for the non-ideal nature of real gases. This is why there are two new constants  $a$  and  $b$ .

The information provided to us indicates that since  $PV = nRT$  solving the differential  $\left(\frac{dT}{dP}\right)_V$  will produce the following;

$$T = \frac{PV}{R} \text{ and therefore,}$$

$$\left(\frac{dT}{dP}\right)_V = \frac{V}{R}$$

Our task now is to carry out the same procedure on the modified van der Waals Equation. First let us expand the expression to isolate for  $T$ .

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$P(V_m - b) + \left(\frac{a}{V_m^2}\right)(V_m - b) = RT$$

Now we will isolate temperature which gives,

$$T = \frac{P(V_m - b)}{R} + \left( \frac{a}{RV_m^2} \right) (V_m - b)$$

Now we must determine the value of the differential,  $\left( \frac{dT}{dP} \right)_V$ .

$$T = \frac{P(V_m - b)}{R} + \left( \frac{a}{RV_m^2} \right) (V_m - b)$$

$$\boxed{\left( \frac{dT}{dP} \right)_V = \frac{V_m - b}{R}}$$

Note that the far right hand side of the expression completely cancels out because there is no  $P$  dependence involved there while  $V$  is being held constant.

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- 2.63.** One mole of a gas at 300 K is compressed isothermally and reversibly from an initial volume of 10 dm<sup>3</sup> to a final volume of 0.2 dm<sup>3</sup>. Calculate the work done on the system if
- the gas is ideal.
  - the equation of state of the gas is  $P(V_m - b) = RT$ , with  $b = 0.03 \text{ dm}^3 \text{ mol}^{-1}$ . Explain the difference between the two values.

**Solution:**

Given:  $n = 1 \text{ mol}$ ,  $T = 300 \text{ K}$ ,  $V_i = 10 \text{ dm}^3$ ,  $V_f = 0.2 \text{ dm}^3$

Required:  $w_{\text{ideal}}$  and see above

This problem will be solved without extensive explanation because we have covered a number of these types of problems already.

- a.** For an *Ideal Gas* under isothermal and reversible conditions:

$$w = -\int_{V_1}^{V_2} P dV$$

$$P = \frac{nRT}{V}$$

$$w = -nRT \ln V \Big|_{V_1}^{V_2}$$

$$w = -nRT \ln \frac{V_2}{V_1}$$

Since the process involves a compression, the work will be done *on* the gas and the work done by the system should be a positive quantity.

$$w = -(1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln \left( \frac{0.2}{10} \right)$$

$$w = 9\,757.954\,584 \text{ J}$$

$$\boxed{w = 9.76 \text{ kJ}}$$

- b.** For a *Real Gas* under the same isothermal and reversible conditions, we will solve the problem using the equation of state for the particular gas. We need to express the work done while using the equation of state. This means that we should first expand and simplify the equation of state if possible.



$$P(V_m - b) = nRT$$

$$P = \frac{nRT}{(V_m - b)}$$

$$w = -\int_{V_1}^{V_2} P dV$$

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{(V_m - b)}$$

Let  $(V_m - b) = x$  and  $dV = dx$  to simplify the integration. Making these substitutions gives,

$$w = -nRT \int_{V_1}^{V_2} \frac{dx}{x}$$

$$w = -nRT \ln(V_m - b) \Big|_{V_1}^{V_2}$$

$$w = -nRT \ln\left(\frac{V_f - b}{V_i - b}\right)$$

$$w = (-1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln\left(\frac{0.2 \text{ dm}^3 - 0.03 \text{ dm}^3}{10.0 \text{ dm}^3 - 0.03 \text{ dm}^3}\right)$$

$$w = (-1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln\left(\frac{0.17 \text{ dm}^3}{9.97 \text{ dm}^3}\right)$$

$$w = 10\,155.839\,38 \text{ J}$$

$$\boxed{w = 10.16 \text{ kJ}}$$

It should be noted that the reason why there is more work done when working with a real gas (as compared to an ideal gas), is because of the larger absolute value of the ratio of free volumes.

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- 2.64.** One mole of a gas at 100 K is compressed isothermally from an initial volume of 20 dm<sup>3</sup> to a final volume of 5 dm<sup>3</sup>. Calculate the work done on the system if
- the gas is ideal.
  - the equation of state is

$$\left( P + \frac{a}{V_m^2} \right) V_m = RT \text{ where } a = 0.384 \text{ m}^6 \text{ Pa mol}^{-1}$$

[This equation is obeyed approximately at low temperatures, whereas  $P(V_m - b) = RT$  (see Problem 2.63) is obeyed more closely at higher temperatures.] Account for the difference between the values in (a) and (b).

**Solution:**

Given:  $n = 1 \text{ mol}$ ,  $T = 100 \text{ K}$ ,  $V_i = 20 \text{ dm}^3$ ,  $V_f = 5 \text{ dm}^3$

Required:  $w_{\text{ideal}}$  and  $w_{\text{real}}$

- a.** This situation is similar to the last problem in that, the gas is being compressed and the system is the component doing the work. This means that the value obtained for work should be positive. We are still working under isothermal conditions!

For the Ideal Gas (please note that we have been solving all problems according to the single mole assumption):

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$w = -\int_{V_i}^{V_f} P dV$$

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$w = -nRT \ln V \Big|_{V_i}^{V_f}$$

$$w = -nRT \ln \frac{V_f}{V_i}$$

$$w = -(1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (100 \text{ K}) \ln \left( \frac{5}{20} \right)$$

$$w = 1152.634447 \text{ J}$$

$$\boxed{w_{\text{ideal}} = 1.15 \text{ kJ}}$$

- b.** For the *Real Gas*:  $\left( P + \frac{a}{V_m^2} \right) V_m = RT$  should be expanded and simplified so that we can execute the same kind of procedure as was done in the first part of this problem.

$$\left(P + \frac{a}{V_m^2}\right)V_m = nRT$$

$$P + \frac{a}{V_m^2} = \frac{nRT}{V_m}$$

$$P = \frac{nRT}{V_m} - \frac{a}{V_m^2}$$

$$w = -\int_{V_i}^{V_f} P dV$$

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} + a \int_{V_i}^{V_f} \frac{dV}{V^2}$$

$$w = -nRT \ln V \Big|_{V_i}^{V_f} + a \left( -\frac{1}{V} \right) \Big|_{V_i}^{V_f}$$

$$w = -nRT \ln \left( \frac{V_f}{V_i} \right) - a \left( \frac{1}{V_f} - \frac{1}{V_i} \right)$$

$$w = -\left(1.0 \text{ mol}\right)\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(100 \text{ K}\right) \ln \left(\frac{5}{20}\right)$$

$$- \left(0.384 \text{ m}^6 \text{ Pa}\right) \left( \frac{1}{5 \text{ dm}^3} - \frac{1}{20 \text{ dm}^3} \right)$$

$$1000 \text{ dm}^3 = 1 \text{ m}^3, \text{ m}^6 = (1 \text{ m}^3)^2, 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}, 1 \text{ atm dm}^3 = 101.325 \text{ J}$$

$$w = (1152.634447 \text{ J}) - \left(0.0576 \frac{\text{m}^6 \text{ Pa}}{\text{dm}^3}\right) \times \frac{1000 \text{ dm}^3}{1 \text{ m}^3}$$

$$w = (1152.634447 \text{ J}) - (57.6 \text{ Pa m}^3)$$

$$w = (1152.634447 - 57.6) \text{ J}$$

$$w = 1095.034447 \text{ J}$$

$$\boxed{w_{\text{real}} = 1.10 \text{ kJ}}$$

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**2.65.** Derive the expression

$$dP = \frac{P dV_m}{V_m - b} - \frac{ab}{V_m^3(V_m - b)} dV_m + \frac{P dT}{T} + \frac{a dT}{V_m^2 T}$$

for 1 mol of a van der Waals gas.

**Solution:**

We are already familiar with the van der Waals expression for a single mole of gas. Now, we will need to use the partial derivatives section of Appendix C in order to generate the corresponding relationship.

Starting with the van der Waals Equation for 1 mole of gas:

Expand  $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$  to form,

$$\left(P + \frac{a}{V_m^2}\right) = \frac{RT}{(V_m - b)}$$

$$P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

The total differential can be written from Appendix C as,

$$dP = \left(\frac{\partial P}{\partial V_m}\right)_T dV_m + \left(\frac{\partial P}{\partial T}\right)_{V_m} dT$$

Since we have already found the total differential for the pressure, we can determine the values of these two partial derivatives.

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{(V_m - b)}$$

$$\left(\frac{\partial P}{\partial V_m}\right)_T = \frac{-1}{(V_m - b)^2} RT + \left(\frac{2a}{V_m^3}\right)$$

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \left(\frac{2a}{V_m^3}\right)$$

Now we can substitute these values into the total derivative to reproduce the derived equation given above.

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \left(\frac{2a}{V_m^3}\right) \text{ and } \left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{(V_m - b)}$$

Substitution of these into

$$dP = \left(\frac{\partial P}{\partial V_m}\right)_T dV_m + \left(\frac{\partial P}{\partial T}\right)_{V_m} dT$$

gives,

$$dP = -\left(\frac{RT}{(V_m - b)^2}\right)dV_m + \left(\frac{2a}{V_m^3}\right)dV_m + \left(\frac{R}{(V_m - b)}\right)dT$$

Remember that:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \text{ so we can actually add back in the pressure term.}$$

For the first two segments of the expression above, the substitution will be as follows;

$$dP = -\left(\frac{\left(P + \frac{a}{V_m^2}\right)\cancel{(V_m - b)}}{(V_m - b)^{\cancel{2}}}\right)dV_m + \left(\frac{2a}{V_m^3}\right)dV_m$$

$$dP = -\left(\frac{P + \frac{a}{V_m^2}}{V_m - b}\right)dV_m + \left(\frac{2a}{V_m^3}\right)dV_m$$

The last segment is slightly tricky because we need to separate the equation again and this will create four segments rather than the original three. Let's try!

$$P = \frac{RT}{(V_m - b)} - \left( \frac{a}{V_m^2} \right)$$

$$\frac{P}{T} = \frac{R}{(V_m - b)} - \left( \frac{a}{TV_m^2} \right)$$

$$\frac{R}{(V_m - b)} = \frac{P}{T} + \frac{a}{TV_m^2}$$

$$dP = \dots\dots\dots + \dots\dots\dots + \left( \frac{R}{(V_m - b)} \right) dT$$

$$dP = \dots\dots\dots + \dots\dots\dots + \left( \frac{P}{T} + \frac{a}{TV_m^2} \right) dT$$

Now everything can be put together to get:

$$dP = - \left( \frac{P + \frac{a}{V_m^2}}{V_m - b} \right) dV_m + \left( \frac{2a}{V_m^3} \right) dV_m + \left( \frac{P}{T} \right) dT + \left( \frac{a}{TV_m^2} \right) dT$$

We can now expand a bit;

$$dP = - \frac{P}{V_m - b} dV_m - \frac{\frac{a}{V_m^2}}{V_m - b} dV_m + \frac{2a}{V_m^3} dV_m + \frac{P}{T} dT + \frac{a}{V_m^2 T} dT$$

$$dP = - \frac{P}{V_m - b} dV - \frac{aV_m - 2a(V_m - b)}{V_m^3 (V_m - b)} + \frac{P}{T} dT + \frac{a}{V_m^2 T} dT$$

$$\boxed{dP = - \frac{P}{V_m - b} dV - \frac{2ab - aV_m}{V_m^3 (V_m - b)} + \frac{P dT}{T} + \frac{a dT}{V_m^2 T}}$$

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- 2.66.** If a substance is burned at constant volume with no heat loss, so that the heat evolved is all used to heat the product gases, the temperature attained is known as the *adiabatic flame temperature*. Calculate this quantity for methane burned at 25 °C in the amount of oxygen required to give complete combustion to CO<sub>2</sub> and H<sub>2</sub>O. Use the data in Appendix D and the following approximate expressions for the heat capacities:

$$C_{P,m}(\text{CO}_2)/\text{J K}^{-1} \text{mol}^{-1} = 44.22 + 8.79 \times 10^{-3} T/\text{K}$$

$$C_{P,m}(\text{H}_2\text{O})/\text{J K}^{-1} \text{mol}^{-1} = 30.54 + 1.03 \times 10^{-2} T/\text{K}$$

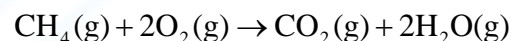
**Solution:**

Given: Appendix D,  $C_{P,m}(\text{CO}_2)/\text{J K}^{-1} \text{mol}^{-1} = 44.22 + 8.79 \times 10^{-3} T/\text{K}$

$$C_{P,m}(\text{H}_2\text{O})/\text{J K}^{-1} \text{mol}^{-1} = 30.54 + 1.03 \times 10^{-2} T/\text{K}$$

Required:  $T$  adiabatic flame temperature

With any problem of this type, it is always important to begin by writing down all of the reactions that will be useful. The balanced reaction for the complete combustion of methane gas is as follows:



Remember from previous problems that we can determine the standard enthalpy change by using the enthalpies of formation for all species involved.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = \Delta_f H^\circ(\text{CO}_2, \text{g}) + 2\Delta_f H^\circ(\text{H}_2\text{O}, \text{g}) - \Delta_f H^\circ(\text{CH}_4, \text{g})$$

By using the enthalpies of formation found in Appendix D, we can calculate this value.

$$\Delta H^\circ = (-393.51 \text{ kJ mol}^{-1}) + (2 \times -241.826 \text{ kJ mol}^{-1}) - (-74.6 \text{ kJ mol}^{-1})$$

$$\Delta H^\circ = -802.562 \text{ kJ mol}^{-1}$$

We have been given the expressions for the heat capacities for both carbon dioxide and gaseous water so we can combine them in order to get the total heat capacity for the products.



$$C_{P,m}(\text{CO}_2) / \text{J K}^{-1} \text{ mol}^{-1} = 44.22 + 8.79 \times 10^{-3} (T / \text{K})$$

$$C_{P,m}(\text{H}_2\text{O}) / \text{J K}^{-1} \text{ mol}^{-1} = 30.54 + 1.03 \times 10^{-2} (T / \text{K})$$

$$C_P(\text{products}) / \text{J K}^{-1} \text{ mol}^{-1} = C_{P,m}(\text{CO}_2) + 2C_{P,m}(\text{H}_2\text{O})$$

$$C_P(\text{products}) / \text{J K}^{-1} \text{ mol}^{-1} = 105.30 + 2.939 \times 10^{-2} (T / \text{K})$$

Since we are working under constant volume, we will need to determine the appropriate values for the heat capacity. Recall that:

$$C_{P,m} - C_{V,m} = R$$

$$C_{V,m} = C_{P,m} - R$$

We can use the expression for the heat absorbed in order to determine the final temperature. Remember that under these conditions, the heat absorbed by the gas will be equal to the standard internal energy change for the reaction. Since we are using the heat capacity given in terms of constant pressure conditions, we will be making the appropriate arrangements to involve the value we solved for initially.

$$q_{V,m} = \int_{T_1}^{T_2} C_{V,m} dT = C_{V,m} (T_2 - T_1)$$

$$q_{V,m} = \int_{298.15}^{T_2/K} (C_{P,m} - R) d(T/K)$$

$$802\,562 \text{ J mol}^{-1} = \int_{298.15}^{T_2/K} (105.30 - 8.3145 + 2.939 \times 10^{-2} (T / \text{K})) d(T / \text{K})$$

$$802\,562 = \int_{298.15}^{T_2/K} (96.9855 + 2.939 \times 10^{-2} (T / \text{K})) d(T / \text{K})$$

$$802\,562 = (96.9855) \Big|_{298.15}^{T_2/K} + \frac{1}{2} (2.939 \times 10^{-2} (T / \text{K}))^2 \Big|_{298.15}^{(T_2/K)}$$

$$802\,562 = 96.9855 \left( \frac{T_2}{\text{K}} - 298.15 \right) + 1.4695 \times 10^{-2} \left( \frac{T_2^2}{\text{K}^2} - 88\,893.422\,5 \right)$$

$$802\,562 = 96.9855 \left( \frac{T_2}{\text{K}} \right) - 28\,916.226\,83 + 1.4695 \times 10^{-2} \left( \frac{T_2}{\text{K}} \right)^2 - 1306.288\,844$$

$$1.4695 \times 10^{-2} \left( \frac{T_2}{\text{K}} \right)^2 + 96.9855 \left( \frac{T_2}{\text{K}} \right) - 832\,784.515\,7 = 0$$

This forms a quadratic equation which can then be solved to determine the adiabatic flame temperature for methane. Let each term correspond to the general quadratic equation given by  $ax^2 + bx + c = 0$ . This means that  $\frac{T_2}{K} = x$  which leads to;

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\frac{T_2}{K} = \frac{-96.9855 \pm \sqrt{(96.9855)^2 - 4(1.4695 \times 10^{-2})(-832\,784.515\,7)}}{2(1.4695 \times 10^{-2})}$$

$$\frac{T_2}{K} = \frac{-96.9855 \pm \sqrt{58\,357.261\,04}}{(2.939 \times 10^{-2})}$$

Using the positive value for the square root we obtain,

$$\frac{T_2}{K} = \frac{-96.9855 + \sqrt{58\,357.261\,04}}{2.939 \times 10^{-2}}$$

$$\frac{T_2}{K} = 4\,919.597\,678$$

$$T_2 = 4\,920\text{ K}$$

$$\boxed{T_{\text{flame}} = 4\,920\text{ K}}$$

The value as calculated may vary by about 20 K lower depending upon how many significant figures we used in the calculation. This value may be reduced by about 170 K under constant pressure condition.

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- 2.67.** Two moles of a gas are compressed isothermally and reversibly, at 300 K, from an initial volume of 10 dm<sup>3</sup> to a final volume of 1 dm<sup>3</sup>. If the equation of state of the gas is  $P(V_m - b) = RT$ , with  $b = 0.04 \text{ dm}^3 \text{ mol}^{-1}$ , calculate the work done on the system,  $\Delta U$ , and  $\Delta H$ .

**Solution:**

Given:  $n = 2 \text{ mol}$ ,  $T = 300 \text{ K}$ ,  $V_i = 10 \text{ dm}^3$ ,  $V_f = 1 \text{ dm}^3$

$$P(V_m - b) = RT, \text{ with } b = 0.04 \text{ dm}^3 \text{ mol}^{-1}$$

Required:  $w$ ,  $\Delta U$ ,  $\Delta H$

We have seen many problems like this one already. Remember that under isothermal conditions, there is no change in temperature. It is also important to note that the process is reversible. Lastly, we are working with a Real Gas which means that we cannot use the Ideal Gas Law.

Since the gas is undergoing a compression, the reversible work *done on* the system is given by:

$$w_{\text{rev}} = -\int_{V_i}^{V_f} P dV$$

using Eq. of state:  $P(V - nb) = nRT$

then  $P = \frac{nRT}{(V - nb)}$  and so,

$$w_{\text{rev}} = -nRT \int_{V_i}^{V_f} \frac{dV}{(V - nb)}$$

$$w_{\text{rev}} = -nRT \ln(V - nb) \Big|_{V_i}^{V_f}$$

$$w_{\text{rev}} = -nRT \ln \left( \frac{V_f - nb}{V_i - nb} \right)$$

$$w_{\text{rev}} = -(2.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln \left( \frac{1 \text{ dm}^3 - (2.0 \text{ mol}) (0.04 \text{ dm}^3 \text{ mol}^{-1})}{10 \text{ dm}^3 - (2.0 \text{ mol}) (0.04 \text{ dm}^3 \text{ mol}^{-1})} \right)$$

$$w_{\text{rev}} = -(2.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln \left( \frac{0.92}{9.92} \right)$$

$$w_{\text{rev}} = 11\,862.801\,99 \text{ J}$$

$$\boxed{w_{\text{rev}} = 11.86 \text{ kJ}}$$

The change in internal energy for a Real Gas is given by Eq. 2.124 and Eq. 2.125:

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV = \frac{n^2 a}{V^2} dV$$

$$\Delta U = \int_{V_i}^{V_f} \frac{n^2 a}{V^2} dV = n^2 a \left( \frac{-1}{V} \right) \Big|_{V_i}^{V_f}$$

$$\Delta U = n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right)$$

Since the constant  $a$  is not involved in the equation of state for this unknown real gas, there will be no change in the internal energy throughout the reaction.

$$\boxed{\Delta U = 0}$$

Eq. 2.127 will then enable us to determine the change in enthalpy.

$$\Delta H = \Delta U + \Delta(PV)$$

We have not been given the pressures corresponding to the system so they must be calculated using the equation of state.

$$P(V - nb) = nRT$$

$$P_i = \frac{nRT}{(V_i - nb)} \text{ and } P_f = \frac{nRT}{(V_f - nb)}$$

$$P_i = \frac{(2.0 \text{ mol})(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{[10 \text{ dm}^3 - (2.0 \text{ mol})0.04 \text{ dm}^3 \text{ mol}^{-1}]}$$

$$P_i = \frac{49.89 \text{ bar dm}^3}{(9.92 \text{ dm}^3)}$$

$$P_i = 5.029 \text{ 233 871 bar}$$

$$P_f = \frac{(2.0 \text{ mol})(0.08315 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{[10 \text{ dm}^3 - (2.0 \text{ mol})0.04 \text{ dm}^3 \text{ mol}^{-1}]}$$

$$P_f = \frac{49.89 \text{ bar dm}^3}{(0.92 \text{ dm}^3)}$$

$$P_f = 54.228 \text{ 260 87 bar}$$

We can now find the value for the  $P$ - $V$  work done and subsequently the change in enthalpy for the reaction.

$$P_i V_i = (5.029 \text{ 233 871 bar})(10.0 \text{ dm}^3)$$

$$P_i V_i = 50.292 \text{ 338 71 bar dm}^3$$

$$1 \text{ bar} = 10^5 \text{ Pa}, 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}, 1 \text{ atm dm}^3 = 101.325 \text{ J}$$

$$P_i V_i = 50.292 \, 338 \, 71 \, \cancel{\text{bar}} \, \text{dm}^3 \times \frac{10^5 \, \cancel{\text{Pa}}}{1 \, \cancel{\text{bar}}} \times \frac{1 \text{ atm}}{1.01325 \times 10^5 \, \cancel{\text{Pa}}}$$

$$P_i V_i = 49.634 \, 679 \, 21 \, \cancel{\text{atm}} \, \text{dm}^3 \times \frac{101.325 \text{ J}}{1 \, \cancel{\text{atm}} \, \text{dm}^3}$$

$$P_i V_i = 5029.233 \, 871 \text{ J}$$

$$P_f V_f = (54.228 \, 260 \, 87 \text{ bar})(1.0 \text{ dm}^3)$$

$$P_f V_f = 54.228 \, 260 \, 87 \text{ bar dm}^3$$

$$P_f V_f = 54.228 \, 260 \, 87 \, \cancel{\text{bar}} \, \text{dm}^3 \times \frac{10^5 \, \cancel{\text{Pa}}}{1 \, \cancel{\text{bar}}} \times \frac{1 \text{ atm}}{1.01325 \times 10^5 \, \cancel{\text{Pa}}}$$

$$P_f V_f = 53.519 \, 132 \, 37 \, \cancel{\text{atm}} \, \text{dm}^3 \times \frac{101.325 \text{ J}}{1 \, \cancel{\text{atm}} \, \text{dm}^3}$$

$$P_f V_f = 5422.826 \, 087 \text{ J}$$

$$\Delta(PV) = P_f V_f - P_i V_i$$

$$\Delta(PV) = (5422.826 \, 087 - 5029.233 \, 871) \text{ J}$$

$$\Delta(PV) = 393.592 \, 216 \text{ J}$$

$$\Delta H = \Delta \mathcal{U} + \Delta(PV)$$

$$\boxed{\Delta H = 394 \text{ J}}$$

The application of the correct number of significant figures gives,

$$\boxed{\Delta H = 4 \times 10^2 \text{ J}}$$

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- 2.68.** Three moles of a gas are compressed isothermally and reversibly, at 300 K, from an initial volume of 20 dm<sup>3</sup> to a final volume of 1 dm<sup>3</sup>. If the equation of state of the gas is

$$\left(P + \frac{n^2 a}{V_m^2}\right) V_m = nRT$$

with  $a = 0.55 \text{ Pa m}^6 \text{ mol}^{-1}$ , calculate the work done,  $\Delta U$ , and  $\Delta H$ .

**Solution:**

Given:  $n = 3 \text{ mol}$ ,  $T = 300 \text{ K}$ ,  $V_i = 20 \text{ dm}^3$ ,  $V_f = 1 \text{ dm}^3$ ,  $\left(P + \frac{n^2 a}{V_m^2}\right) V_m = nRT$

Required:  $w$ ,  $\Delta U$ ,  $\Delta H$

We will solve this problem in the exact same way as problem 2.67 was done. Since the two problems are extremely similar, no additional explanation will be provided.

$$w_{\text{rev}} = -\int_{V_i}^{V_f} P dV$$

using Eq. of state:  $\left(P + \frac{n^2 a}{V_m^2}\right) V_m = nRT$

then  $PV_m + \frac{n^2 a}{V_m} = nRT$  and so  $P = \frac{nRT}{V_m} - \frac{n^2 a}{V_m^2}$

$$w_{\text{rev}} = -\int_{V_i}^{V_f} \left( \frac{nRT}{V_m} - \frac{n^2 a}{V_m^2} \right) dV_m$$

$$w_{\text{rev}} = -nRT \ln V_m \Big|_{V_i}^{V_f} + n^2 a \left( -\frac{1}{V_m} \right) \Big|_{V_i}^{V_f}$$

$$w_{\text{rev}} = -nRT \ln \frac{V_f}{V_i} + n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right)$$

$$w_{\text{rev}} = -\left(3.0 \text{ mol}\right)\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(300 \text{ K}\right) \ln\left(\frac{1}{20}\right) \\ + \left(3.0 \text{ mol}\right)^2 \left(0.55 \text{ Pa m}^6 \text{ mol}^{-1}\right) \left(\frac{1}{20 \times 10^{-3} \text{ m}^3} - \frac{1}{10^{-3} \text{ m}^3}\right)$$

$$w_{\text{rev}} = 22\,417.21439 \text{ J} - 4702.5 \text{ Pa m}^3$$

$$w_{\text{rev}} = 22\,417.21439 \text{ J} - 4702.5 \text{ J}$$

$$w_{\text{rev}} = 17\,714.714\,39 \text{ J}$$

$$w_{\text{rev}} = 17.71 \text{ kJ}$$



$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV = \frac{n^2 a}{V^2} dV$$

$$\Delta U = \int_{V_i}^{V_f} \frac{n^2 a}{V^2} dV = n^2 a \left( \frac{-1}{V} \right) \Bigg|_{V_i}^{V_f}$$

$$\Delta U = n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right)$$

$$\Delta U = (3.00 \text{ mol})^2 (0.55 \text{ Pa m}^6 \text{ mol}^{-1}) \left( \frac{1}{20 \times 10^{-3} \text{ m}^3} - \frac{1}{10^{-3} \text{ m}^3} \right)$$

$$\Delta U = -4702.5 \text{ Pa m}^3$$

$$\Delta U = -4702.5 \text{ J}$$

$$\boxed{\Delta U = -4.70 \text{ kJ}}$$

$$\left( P + \frac{n^2 a}{V_m^2} \right) V_m = nRT$$

$$P = \frac{nRT}{V_m} - \frac{n^2 a}{V_m^2}$$

$$P_i = \frac{nRT}{V_i} - \frac{n^2 a}{V_i^2} \text{ and } P_f = \frac{nRT}{V_f} - \frac{n^2 a}{V_f^2}$$

$$P_i = \frac{(3.0 \text{ mol})(8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(20 \times 10^{-3} \text{ m}^3)} - \frac{(3.0^2 \text{ mol})(0.55 \text{ Pa m}^6 \text{ mol}^{-1})}{(20 \times 10^{-3} \text{ m}^3)^2}$$

$$P_i = 374\,152.5 \text{ Pa} - 12\,375 \text{ Pa}$$

$$P_i = 361\,777.5 \text{ Pa}$$

$$P_f = \frac{(3.0 \text{ mol})(8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(1.0 \times 10^{-3} \text{ dm}^3)} - \frac{(3.0^2 \text{ mol})(0.55 \text{ Pa m}^6 \text{ mol}^{-1})}{(1.0 \times 10^{-3} \text{ m}^3)^2}$$

$$P_f = 7\,483\,050 \text{ Pa} - 4\,950\,000 \text{ Pa}$$

$$P_f = 2\,533\,050 \text{ Pa}$$

$$P_i V_i = (361\,777.5 \text{ Pa})(20 \times 10^{-3} \text{ m}^3)$$

$$P_i V_i = 7\,235.55 \text{ Pa m}^3$$

$$P_i V_i = 7\,235.55 \text{ J}$$

$$P_f V_f = (2\,533\,050 \text{ Pa})(1.0 \times 10^{-3} \text{ dm}^3)$$

$$P_f V_f = 2\,533.05 \text{ Pa m}^3$$

$$P_f V_f = 2\,533.05 \text{ J}$$

$$\Delta(PV) = P_f V_f - P_i V_i$$

$$\Delta(PV) = (2\,533.05 - 7\,235.55) \text{ J}$$

$$\Delta(PV) = -4702.5 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = (-4702.5 - 4702.5) \text{ J}$$

$$\Delta H = -9405 \text{ J}$$

$$\boxed{\Delta H = -9.41 \text{ kJ}}$$

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**2.69.** One mole of a van der Waals gas at 300 K is compressed isothermally and reversibly from  $60 \text{ dm}^3$  to  $20 \text{ dm}^3$ . If the constants in the van der Waals equation are

$$a = 0.556 \text{ Pa m}^6 \text{ mol}^{-1} \text{ and } b = 0.064 \text{ dm}^3 \text{ mol}^{-1}$$

calculate  $w_{\text{rev}}$ ,  $\Delta U$ , and  $\Delta H$ .

**Solution:**

Given: van der Waals gas:  $n = 1 \text{ mol}$ ,  $T = 300 \text{ K}$ ,  $V_i = 60 \text{ dm}^3$ ,  $V_f = 20 \text{ dm}^3$

$$a = 0.556 \text{ Pa m}^6 \text{ mol}^{-1}, \quad b = 0.064 \text{ dm}^3 \text{ mol}^{-1}$$

Required:  $w_{\text{rev}}$ ,  $\Delta U$ ,  $\Delta H$

The reversible work for a van der Waals gas is given by Eq. 2.122 and Eq. 2.123:

$$w_{\text{rev}} = -\int_{V_i}^{V_f} P dV$$

using Van der Waals Eq:  $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

$$w_{\text{rev}} = -\int_{V_i}^{V_f} \left( \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \right) dV$$

$$w_{\text{rev}} = -nRT \ln(V - nb) \Big|_{V_i}^{V_f} + n^2 a \left( -\frac{1}{V} \right) \Big|_{V_i}^{V_f}$$

$$w_{\text{rev}} = -nRT \ln \left( \frac{V_f - nb}{V_i - nb} \right) + n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right)$$

$$w_{\text{rev}} = -(1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln \left( \frac{20 - 0.064}{60 - 0.064} \right) \\ + (1.0 \text{ mol})^2 (0.556 \text{ Pa m}^6 \text{ mol}^{-1}) \left( \frac{1}{60 \times 10^{-3} \text{ m}^3} - \frac{1}{20 \times 10^{-3} \text{ m}^3} \right)$$

$$w_{\text{rev}} = 2\,727.122\,887 \text{ J}$$

$$\boxed{w_{\text{rev}} = 2.73 \text{ kJ}}$$

Recall that from Eq. 2.124 and Eq. 2.125 we can solve for the change in internal energy:

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV = \frac{n^2 a}{V^2} dV$$

$$\Delta U = \int_{V_i}^{V_f} \frac{n^2 a}{V^2} dV = n^2 a \left( \frac{-1}{V} \right) \Big|_{V_i}^{V_f}$$

$$\Delta U = n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right)$$

$$\Delta U = (1.00 \text{ mol})^2 (0.556 \text{ Pa m}^6 \text{ mol}^{-1}) \left( \frac{1}{60 \times 10^{-3} \text{ m}^3} - \frac{1}{20 \times 10^{-3} \text{ m}^3} \right)$$

$$\Delta U = -18.533 \text{ 3 Pa m}^3$$

$$\Delta U = -18.533 \text{ 3 J}$$

$$\boxed{\Delta U = -18.5 \text{ J}}$$

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$P_i = \frac{nRT}{(V_i - nb)} - \frac{n^2 a}{V_i^2} \text{ and } P_f = \frac{nRT}{(V_f - nb)} - \frac{n^2 a}{V_f^2}$$

$$P_i = \frac{(1.0 \text{ mol})(8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{[(60 - 0.064) \times 10^{-3}] \text{ m}^3} - \frac{(1.0^2 \text{ mol})(0.556 \text{ Pa m}^6 \text{ mol}^{-1})}{(60 \times 10^{-3} \text{ m}^3)^2}$$

$$P_i = 41\,459.669 \text{ 13 Pa}$$

$$P_f = \frac{(1.0 \text{ mol})(8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{[(20 - 0.064) \times 10^{-3}] \text{ m}^3} - \frac{(1.0^2 \text{ mol})(0.556 \text{ Pa m}^6 \text{ mol}^{-1})}{(20 \times 10^{-3} \text{ m}^3)^2}$$

$$P_f = 123\,727.877 \text{ 2 Pa}$$

$$P_i V_i = (41\,459.669\,13\text{ Pa})(60 \times 10^{-3}\text{ m}^3)$$

$$P_i V_i = 2\,487.580\,148\text{ Pa m}^3$$

$$P_i V_i = 2\,487.580\,148\text{ J}$$

$$P_f V_f = (123\,727.877\,2\text{ Pa})(20 \times 10^{-3}\text{ m}^3)$$

$$P_f V_f = 2\,474.557\,544\text{ Pa m}^3$$

$$P_f V_f = 2\,474.557\,544\text{ J}$$

$$\Delta(PV) = P_f V_f - P_i V_i$$

$$\Delta(PV) = (2\,474.557\,544 - 2\,487.580\,148)\text{ J}$$

$$\Delta(PV) = -13.022\,604\text{ J}$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = (-18.533\,3 - 13.022\,604)\text{ J}$$

$$\Delta H = -31.555\,904\text{ J}$$

$$\boxed{\Delta H = -31.56\text{ J}}$$

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**2.70.** Show that the Joule-Thomson coefficient  $\mu$  can be written as:

$$\mu = -\frac{1}{C_p} \left( \frac{\partial H}{\partial P} \right)_T$$

Then, for a van der Waals gas for which  $\mu$  can be written as:

$$\mu = \frac{2a/RT - b}{C_p}$$

calculate  $\Delta H$  for the isothermal compression of 1.00 mol of the gas at 300 K from 1 bar to 100 bar.

**Solution:**

Given:  $n = 1.00$  mol,  $T = 300$  K,  $P_i = 1$  bar,  $P_f = 100$  bar

Required:  $\mu$ ,  $\Delta H$

From Eqs. 2.108 and 2.110 we can see that;

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H \approx \frac{\Delta T}{\Delta P}$$

This value is equal to zero for an Ideal Gas but it may be either positive or negative for a Real Gas. When there is expansion taking place, the change in pressure will be negative (cooling expansion: here the change in temperature is also negative allowing the Joule-Thomson coefficient to be positive).

Conversely, a negative  $\mu$  corresponds to a rise in temperature upon expansion. This is interesting to note because most gases under regular temperatures will cool when they are able to expand. Since the Joule-Thomson expansion occurs at constant enthalpy, the total differential will be:

$$dH = \left( \frac{\partial H}{\partial P} \right)_T dP + \left( \frac{\partial H}{\partial T} \right)_P dT = 0$$

It follows that:

$$\left( \frac{\partial H}{\partial P} \right)_T = - \left( \frac{\partial H}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_H = -C_{p,\mu}$$

We have seen previously that for an ideal gas, the Joule-Thomson coefficient is equal to zero. This also indicates that the enthalpy is independent of pressure. For real gases, we will see that the enthalpy shows some variation with pressure.

Since  $\mu = \left(\frac{\partial T}{\partial P}\right)_H$ , we can use this in order to rearrange the expression given above.

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = -C_{P,\mu}$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial T}{\partial H}\right)_P$$

it follows that,  $\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{-1}{C_P}\right)}$

We are given that:  $\mu = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T = \frac{2a/RT - b}{C_P}$  which then means that we determine the enthalpy change for the isothermal compression

by using the expression for the total differential. Take note that in Chapter 1 there is a table (Table 1.5) which provides the Van der Waals constants for many gases. For simplicity, we will assume that we are working with hydrogen gas. (This is a good choice since  $\mu$  for  $H_2$  is positive.)



$$a = 0.0248 \text{ Pa m}^6 \text{ mol}^{-2}$$

$$b = 0.0266 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

$$dH = \left( \frac{\partial H}{\partial P} \right)_T dP + \left( \frac{\partial H}{\partial T} \right)_P dT = 0$$

$$dH = \left( \frac{2a}{RT} - b \right) dP + \frac{1}{C_p} dT = 0$$

Assuming  $C_p$  to be independent of temperature,

$$dH = \left( \frac{2a}{RT} - b \right) dP$$

$$\int dH = - \int_{P_i}^{P_f} \left( \frac{2a}{RT} - b \right) dP$$

$$\Delta H = - \left( \frac{2a}{RT} - b \right) (P_f - P_i)$$

$$\Delta H = \left( b - \frac{2a}{RT} \right) (P_f - P_i)$$

$$\Delta H = \left( 0.0266 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} - \frac{2(0.0248 \text{ Pa m}^6 \text{ mol}^{-2})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} \right) (100 - 1) \text{ bar}$$

$$1 \text{ bar} = 10^5 \text{ Pa}, 1 \text{ Pa m}^3 = 1 \text{ J}$$

$$\Delta H = \left( 0.0266 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} - \frac{2(0.0248 \text{ m}^6 \text{ mol}^{-2})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} \right) (100 - 1) \times 10^5 \text{ Pa}$$

$$\Delta H = (6.715 \ 060 \ 036 \times 10^{-6}) \text{ m}^3 \text{ mol}^{-1} \times 99 \times 10^5 \text{ Pa}$$

$$\Delta H = 66.479 \ 094 \ 35 \text{ J mol}^{-1}$$

$$\Delta H = 66.5 \text{ J mol}^{-1}$$

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CHAPTER

# 3

## The Second and Third Laws of Thermodynamics

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# Physical Chemistry

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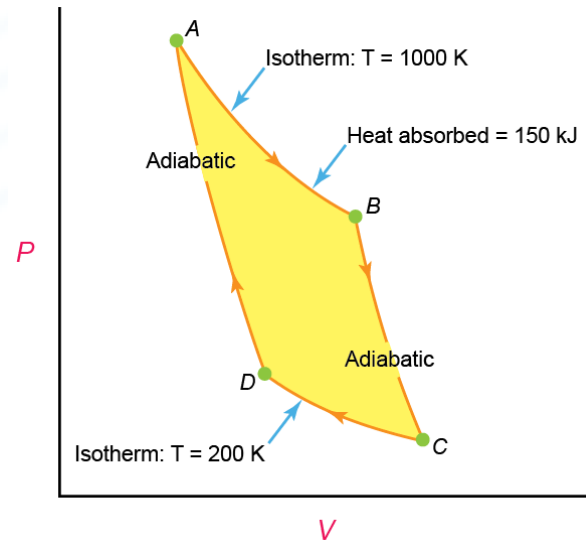
# Problems and Solutions

### Chapter 3

*\*problems with an asterisk are slightly more demanding*

#### The Carnot Cycle (see also Section 3.1)

3.1. The accompanying diagram represents a reversible Carnot cycle for an ideal gas:



- What is the thermodynamic efficiency of the engine?
- How much heat is rejected at the lower temperature,  $200\text{ K}$ , during the isothermal compression?
- What is the entropy increase during the isothermal expansion at  $1000\text{ K}$ ?
- What is the entropy decrease during the isothermal compression at  $200\text{ K}$ ?
- What is the overall entropy change for the entire cycle?
- What is the increase in Gibbs energy during the process  $A \rightarrow B$ ?

[Solution](#)

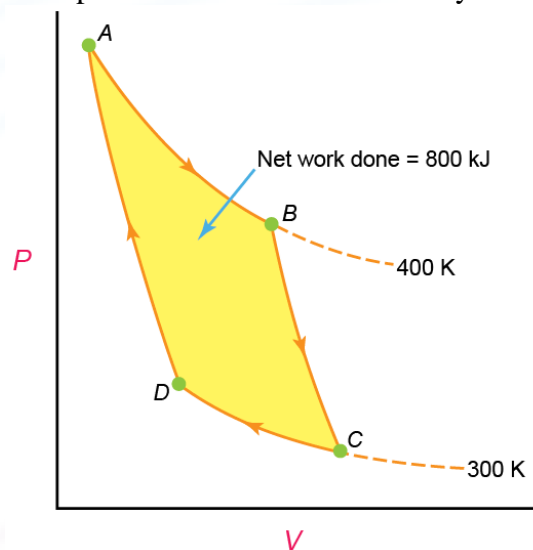
3.2. An engine operates between  $125\text{ }^{\circ}\text{C}$  and  $40\text{ }^{\circ}\text{C}$ . What is the minimum amount of heat that must be withdrawn from the reservoir to obtain  $1500\text{ J}$  of work?

[Solution](#)

- 3.3.** a. Figure 3.2 shows a Carnot cycle in the form of a pressure-volume diagram. Sketch the corresponding entropy-temperature diagram, labeling the individual steps  $A \rightarrow B$  (isotherm at  $T_h$ ),  $B \rightarrow C$  (adiabatic),  $C \rightarrow D$  (isotherm at  $T_c$ ), and  $D \rightarrow A$  (adiabatic).  
 b. Suppose that a reversible Carnot engine operates between 300 K and a higher temperature  $T_h$ . If the engine produces 10 kJ of work per cycle and the entropy change in the isothermal expansion at  $T_h$  is  $100 \text{ J K}^{-1}$ , what are  $q_h$ ,  $q_c$ , and  $T_h$ ?

[Solution](#)

- 3.4.** The following diagram represents a reversible Carnot cycle for an ideal gas:



- What is the thermodynamic efficiency of the engine?
- How much heat is absorbed at 400 K?
- How much heat is rejected at 300 K?
- What is the entropy change in the process  $A \rightarrow B$ ?
- What is the entropy change in the entire cycle?
- What is the Gibbs energy change in the process  $A \rightarrow B$ ?
- In order for the engine to perform 2 kJ of work, how much heat must be absorbed?

[Solution](#)

- 3.5. Suppose that an iceberg weighing  $10^9$  kg were to drift into a part of the ocean where the temperature is  $20^\circ\text{C}$ . What is the maximum amount of work that could be generated while the iceberg is melting? Assume the temperature of the iceberg to be  $0^\circ\text{C}$ . The latent heat of fusion of ice is  $6.025\text{ kJ mol}^{-1}$ .

If the process occurred in one day, what would be the power produced?

[Solution](#)

- 3.6. Show that the change in the internal energy of an ideal gas during an isothermal expansion is zero, i.e.,  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ .

Compare this result to Eq. 3.148 for a van der Waals gas.

[Solution](#)

### Entropy Changes

- 3.7. Calculate the entropies of vaporization in  $\text{J K}^{-1} \text{mol}^{-1}$  of the following substances, from their boiling points and enthalpies of vaporization:

	Boiling Point/K	$\Delta_{\text{vap}}H/\text{kJ mol}^{-1}$
$\text{C}_6\text{H}_6$	353	30.8
$\text{CHCl}_3$	334	29.4
$\text{H}_2\text{O}$	373	40.6
$\text{C}_2\text{H}_5\text{OH}$	351	38.5

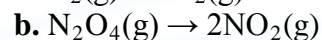
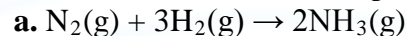
In terms of the structures of the liquids, suggest reasons for the higher values observed for  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_5\text{OH}$ .

[Solution](#)

- 3.8. Calculate the standard entropies of formation of (a) liquid methanol and (b) solid urea, making use of the absolute entropies listed in Table 3.2 (p. 120).

[Solution](#)

**3.9.** Calculate the standard entropies for the following reactions at 25 °C:



[Solution](#)

**3.10.** Calculate the standard entropy for the dissociation of  $\text{H}_2(\text{g})$  into atomic hydrogen  $2[\text{H}(\text{g})]$  at 298.15 K and 1273.15 K.  $C_p^\circ/\text{J K}^{-1} \text{mol}^{-1}$ :  $\text{H}_2(\text{g})$ , 28.824;  $\text{H}(\text{g})$ , 20.784.

[Solution](#)

**3.11.** One mole of an ideal gas, with  $C_{V,m} = \frac{3}{2}R$ , is heated (a) at constant pressure and (b) at constant volume, from 298 K to 353 K. Calculate  $\Delta S$  for the system in each case.

[Solution](#)

**3.12.** One mole each of  $\text{N}_2$  and  $\text{O}_2$  and  $\frac{1}{2}$  mol of  $\text{H}_2$ , at 25 °C and 1 atm pressure, are mixed isothermally; the final total pressure is 1 atm. Calculate  $\Delta S$ , on the assumption of ideal behavior.

[Solution](#)

**3.13.** Initially 1 mol of  $\text{O}_2$  is contained in a 1-liter vessel, and 5 mol of  $\text{N}_2$  are in a 2-liter vessel; the two vessels are connected by a tube with a stopcock. If the stopcock is opened and the gases mix, what is the entropy change?

[Solution](#)

**3.14.** Calculate the entropy of mixing per mole of air, taking the composition by volume to be 79%  $\text{N}_2$ , 20%  $\text{O}_2$ , and 1% Ar.

[Solution](#)

**3.15.** From the data given in Table 3.2 (p. 120), calculate the standard entropy of formation  $\Delta_f S^\circ$  of liquid ethanol at 25 °C.

[Solution](#)

- 3.16.** a. One mole of an ideal gas at 25 °C is allowed to expand reversibly and isothermally from 1 dm<sup>3</sup> to 10 dm<sup>3</sup>. What is  $\Delta S$  for the gas, and what is  $\Delta S$  for its surroundings?  
b. The same gas is expanded adiabatically and irreversibly from 1 dm<sup>3</sup> to 10 dm<sup>3</sup> with no work done. What is the final temperature of the gas? What is  $\Delta S$  for the gas, and what is  $\Delta S$  for the surroundings? What is the net  $\Delta S$ ?

[Solution](#)

- 3.17.** One mole of liquid water at 0.00 °C and 1 atm pressure is turned into steam at 100.0 °C and 1 atm pressure by the following two paths:  
a. Heated at constant pressure to 100.0°C, and allowed to boil into steam ( $\Delta_{\text{vap}}H^\circ = 40.67 \text{ J mol}^{-1}$  at this temperature).  
b. Pressure lowered to 0.006 02 atm so that water evaporates to steam at 0 °C ( $\Delta_{\text{vap}}H^\circ = 44.92 \text{ J mol}^{-1}$  at this temperature), heated at the constant pressure of 0.006 02 atm to 100.0 °C, and compressed at 100.0 °C to 1 atm pressure.  
Calculate the entropy change along each path and verify that they are the same, thus proving that  $\Delta S^\circ$  is a state property. The  $C_{P,m}$  for liquid water and water vapor can be found in Table 2.1. [The paths and the enthalpies of vaporization are adapted from Table 6.1, Gordon M. Barrow, *Physical Chemistry*, 5th Ed., New York: McGraw-Hill, 1988.]

[Solution](#)

- 3.18.** Predict the signs of the entropy changes in the following reactions when they occur in aqueous solution.  
a. Hydrolysis of urea:  $\text{H}_2\text{NCONH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3$   
b.  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$   
c.  $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$   
d.  $\text{CH}_2\text{BrCOOCH}_3 + \text{S}_2\text{O}_3^{2-} \rightarrow \text{CH}_2(\text{S}_2\text{O}_3^-)\text{COOCH}_3 + \text{Br}^-$

[Solution](#)

- 3.19.** Obtain a general expression, in terms of the molar heat capacity  $C_{P,m}$  and temperature  $T_1$  and  $T_2$ , for the entropy increase of  $n$  mol of a gas (not necessarily ideal) that is heated at constant pressure so that its temperature changes from  $T_1$  to  $T_2$ . To what does your expression reduce if the gas is ideal?

[Solution](#)

- 3.20.** Initially 5 mol of an ideal gas, with  $C_{V,m} = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , are at a volume of 5 dm<sup>3</sup> and a temperature of 300 K. If the gas is heated to 373 K and the volume changed to 10 dm<sup>3</sup>, what is the entropy change?

[Solution](#)



- \*3.21.** At 100 °C 200 g of mercury are added to 80 g of water at 20 °C in a vessel that has a water equivalent of 20 g. The specific heat capacities of water and mercury may be taken as constant at 4.18 and 0.140 J K<sup>-1</sup> g<sup>-1</sup>, respectively. Calculate the entropy change of (a) the mercury; (b) the water and vessel; (c) the mercury, water, and vessel together.

[Solution](#)

- \*3.22.** At 0 °C 20 g of ice are added to 50 g of water at 30°C in a vessel that has a water equivalent of 20 g. Calculate the entropy changes in the system and in the surroundings. The heat of fusion of ice at 0 °C is 6.02 kJ mol<sup>-1</sup>, and the specific heat capacities of water and ice may be taken as constant at 4.184 and 2.094 J K<sup>-1</sup> g<sup>-1</sup>, respectively, and independent of temperature.

[Solution](#)

- \*3.23.** Calculate the increase in entropy of 1 mol of nitrogen if it is heated from 300 K to 1000 K at a constant pressure of 1 atm; use the  $C_P$  data in Table 2.1.

[Solution](#)

- \*3.24.** The entropy change for the isothermal expansion of an ideal gas at 300 K from a particular state *A* to a state *B* is 50 J K<sup>-1</sup>. When an expansion was performed, the work done by the system was 6 kJ. Was the process reversible or irreversible? If the latter, calculate the *degree of irreversibility* (i.e., the ratio of the work done to the reversible work).

[Solution](#)

- 3.25.** One mole of water is placed in surroundings at -3 °C, but at first it does not freeze (it remains as supercooled water). Suddenly it freezes. Calculate the entropy change in the system during the freezing, making use of the following data:

$$C_{P,m}(\text{water}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{P,m}(\text{ice}) = 37.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_f H(\text{ice} \rightarrow \text{water}) = 6.01 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}$$

The two  $C_P$  values can be assumed to be independent of temperature. Also, calculate the entropy change in the surroundings, and the net entropy change in the system and surroundings.

[Solution](#)



- 3.26.** 200 cm<sup>3</sup> of a 0.5 m solution of sucrose is diluted to 1 dm<sup>3</sup> by the addition of 800 cm<sup>3</sup> of water. Assume ideal behavior and calculate the entropy change.

[Solution](#)

- 3.27.** One liter of a 0.1 *M* solution of a substance A is added to 3 liters of a 0.05 *M* solution of a substance B. Assume ideal behavior and calculate the entropy of mixing.

[Solution](#)

- 3.28.** Ten moles of water at 60 °C are mixed with an equal amount of water at 20 °C. Neglect any heat exchange with the surroundings and calculate the entropy change. The heat capacity of water may be taken to be 75.3 J K<sup>-1</sup> mol<sup>-1</sup> and independent of temperature.

[Solution](#)

- 3.29.** A vessel is divided by a partition into two compartments. One side contains 5 moles O<sub>2</sub> at 1 atm pressure; the other, 5 moles N<sub>2</sub> at 1 atm pressure. Calculate the entropy change when the partition is removed.

[Solution](#)

- 3.30.** One mole of liquid water at 0 °C is placed in a freezer having a temperature of -12 °C. The water freezes and the ice cools to -12 °C. Making use of the data given in Problem 3.25, calculate the change in entropy in the system and in surroundings (the freezer), and the net entropy change.

[Solution](#)

- 3.31.** One mole of liquid water at 0 °C is placed in a freezer which is maintained at -10 °C. Carry out the same calculations as for Problem 3.30.

[Solution](#)

- 3.32.** Two moles of water at 60 °C are added to 4 mol of water at 20 °C. Calculate the entropy change, assuming that there is no loss of heat to the surroundings. The heat capacity of water is 75.3 J K<sup>-1</sup> mol<sup>-1</sup>.

[Solution](#)

- 3.33.** One mole of an ideal gas is initially at 10 bar and 298 K. It is allowed to expand against a constant external pressure of 2 bar to a final pressure of 2 bar. During this process, the temperature of the gas falls to 253.2 K. Find  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S_{\text{therm}}$ , and  $\Delta S_{\text{univ}}$  for the process. Assume that the thermal surroundings remain at 298 K throughout. Devise at least three different paths to accomplish this change and show that no matter which path is used, the desired values are the same.

[Solution](#)

- 3.34.** Five moles of water at 50 °C are placed in a refrigerator maintained at 3 °C. Calculate  $\Delta S$  for the system and for the environment, and the net entropy change, taking  $C_P$  for water at 75.3 J K<sup>-1</sup> mol<sup>-1</sup> and independent of temperature.

[Solution](#)

- 3.35.** Problem 2.32 of Chapter 2 was concerned with dropping (a) one ice cube, (b) 10 ice cubes, each weighing 100 g, into 1 kg of water at 20 °C. Calculate the entropy change in each case. ( $\Delta H_{\text{fus}}$  of ice at 0 °C is 6.026 kJ mol<sup>-1</sup>;  $C_{P,m}$  for water is 75.3 J K<sup>-1</sup> mol<sup>-1</sup>.)

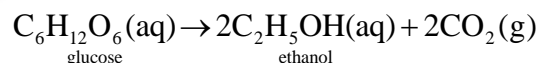
[Solution](#)

- 3.36.** The absolute entropy of nitrogen at its vaporization point of 77.32 K and exactly 1 bar is 151.94 J K<sup>-1</sup> mol<sup>-1</sup>. Using the expression for  $C_{P,m}$  for nitrogen given in Table 2.1, find the entropy of the gas at 800.0 K and 1 bar.

[Solution](#)

### Gibbs and Helmholtz Energies

- 3.37.** Calculate  $\Delta G^\circ$  at 25 °C for the following fermentation reaction:



The standard Gibbs energies of formation of glucose, ethanol, and carbon dioxide are given in Appendix D. Also use the data in Appendix D to calculate  $\Delta S^\circ$  for the fermentation reaction.

[Solution](#)

- 3.38.** The latent heat of vaporization of water at 100 °C is 40.6 kJ mol<sup>-1</sup> and when 1 mol of water is vaporized at 100 °C and 1 atm pressure, the volume increase is 30.19 dm<sup>3</sup>. Calculate the work done by the system, the change in internal energy  $\Delta U$ , the change in Gibbs energy  $\Delta G$  and the entropy change  $\Delta S$ .

[Solution](#)

- 3.39.** On pages 115–116 we worked out the  $\Delta S$  values for the freezing of water at 0 °C and at –10 °C. What are the corresponding  $\Delta G$  values?

[Solution](#)

- 3.40.** At 25 °C 1 mol of an ideal gas is expanded isothermally from 2 to 20 dm<sup>3</sup>. Calculate  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$ , and  $\Delta G$ . Do the values depend on whether the process is reversible or irreversible?

[Solution](#)

- 3.41.** The values of  $\Delta H$  and  $\Delta S$  for a chemical reaction are  $-85.2 \text{ kJ mol}^{-1}$  and  $-170.2 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, and the values can be taken to be independent of temperature.
- a.** Calculate  $\Delta G$  for the reaction at (a) 300 K, (b) 600 K, and (c) 1000 K.
- b.** At what temperature would  $\Delta G$  be zero?

[Solution](#)

- 3.42.** The standard Gibbs energy for the combustion,  $\Delta_c G^\circ$ , of methane has been measured as  $-815.04 \text{ kJ mol}^{-1}$  at 25.0 °C and  $-802.57 \text{ kJ mol}^{-1}$  at 75.0 °C. Assuming that Eq. 3.169 applies and that  $\Delta_c G^\circ$  changes linearly with temperature in this range, estimate the enthalpy of combustion at the midpoint of this temperature range, i.e., 50.0 °C.

[Solution](#)

- 3.43.** The heat of vaporization of water at 25 °C is  $44.01 \text{ kJ mol}^{-1}$ , and the equilibrium vapor pressure at that temperature is 0.0313 atm. Calculate  $\Delta S$ ,  $\Delta H$ , and  $\Delta G$  when 1 mol of liquid water at 25 °C is converted into vapor at 25 °C and a pressure of  $10^{-5}$  atm, assuming the vapor to behave ideally.

[Solution](#)

- 3.44.** For each of the following processes, state which of the quantities  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$ , and  $\Delta G$  are equal to zero:
- a.** Isothermal reversible expansion of an ideal gas.
- b.** Adiabatic reversible expansion of a nonideal gas.
- c.** Adiabatic expansion of an ideal gas through a throttling valve.

- d. Adiabatic expansion of a nonideal gas through a throttling valve.
- e. Vaporization of liquid water at 80 °C and 1 bar pressure.
- f. Vaporization of liquid water at 100 °C and 1 bar pressure.
- g. Reaction between  $\text{H}_2$  and  $\text{O}_2$  in a thermally insulated bomb.
- h. Reaction between  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  in dilute aqueous solution at constant temperature and pressure.

[Solution](#)

- 3.45.** Calculate the change  $\Delta G_m$  in the Gibbs energy of 1 mol of liquid mercury initially at 1 bar pressure if a pressure of 1000 bar is applied to it. The process occurs at the constant temperature of 25 °C, and the mercury may be assumed to be incompressible and to have a density of  $13.5 \text{ g cm}^{-3}$ .

[Solution](#)

- 3.46.** The entropy of argon is given to a good approximation by the expression

$$S_m/\text{J K}^{-1} \text{ mol}^{-1} = 36.36 + 20.79 \ln(T/\text{K})$$

Calculate the change in Gibbs energy of 1 mol of argon if it is heated at constant pressure from 25 °C to 50 °C.

[Solution](#)

- 3.47.** Calculate the absolute entropy of  $\text{SO}_2(\text{g})$  at 300.0 K and 1 bar given the following information:  $S^\circ(15.0 \text{ K}) = 1.26 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $C_{P,m}(\text{s}) = 32.65 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T_{\text{fus}} = 197.64 \text{ K}$ ,  $\Delta_{\text{fus}}H^\circ = 7\,402 \text{ J mol}^{-1}$ ,  $C_{P,m}(\text{l}) = 87.20 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T_{\text{vap}} = 263.08 \text{ K}$ ,  $\Delta_{\text{vap}}H^\circ = 24\,937 \text{ J mol}^{-1}$ ,  $C_{P,m}(\text{g}) = 39.88 \text{ J K}^{-1} \text{ mol}^{-1}$ .

[Solution](#)

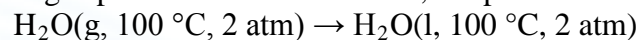
- 3.48.** Initially at 300 K and 1 bar pressure, 1 mol of an ideal gas undergoes an irreversible isothermal expansion in which its volume is doubled, and the work it performs is  $500 \text{ J mol}^{-1}$ . What are the values of  $q$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$ ? What would  $q$  and  $w$  be if the expansion occurred reversibly?

[Solution](#)

- \*3.49.** At 100 °C 1 mol of liquid water is allowed to expand isothermally into an evacuated vessel of such a volume that the final pressure is 0.5 atm. The amount of heat absorbed in the process was found to be  $30 \text{ kJ mol}^{-1}$ . What are  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ ?

[Solution](#)

- \*3.50.** Water vapor can be maintained at 100 °C and 2 atm pressure for a time, but it is in a state of metastable equilibrium and is said to be supersaturated. Such a system will undergo spontaneous condensation; the process is:



Calculate  $\Delta H_m$ ,  $\Delta S_m$ , and  $\Delta G_m$ . The molar enthalpy of vaporization  $\Delta_{\text{vap}}H_m$  is 40.60 kJ mol<sup>-1</sup>; assume the vapor to behave ideally and liquid water to be incompressible.

[Solution](#)

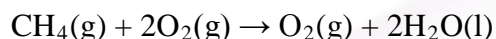
- \*3.51.** Initially at 300 K and 10 atm pressure, 1 mol of a gas is allowed to expand adiabatically against a constant pressure of 4 atm until equilibrium is reached. Assume the gas to be ideal with:

$$C_{P,m} / \text{J K}^{-1} \text{ mol}^{-1} = 28.58 + 1.76 \times 10^{-2} T/\text{K}$$

and calculate  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$ .

[Solution](#)

- 3.52.** Calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  for the reaction



making use of the data in Appendix D.

[Solution](#)

- 3.53.** The following is a set of special conditions:

- True only for an ideal gas.
- True only for a reversible process.
- True only if  $S$  is the total entropy (system + surroundings).
- True only for an isothermal process occurring at constant pressure.
- True only for an isothermal process occurring at constant volume.

Consider each of the following statements, and indicate which of the above conditions must apply in order for the statement to be true:

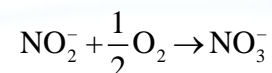
- $\Delta U = 0$  for an isothermal process.
- $\Delta H = 0$  for an isothermal process.
- The total  $\Delta S = 0$  for an adiabatic process.
- $\Delta S >$  ☐ 0 for a spontaneous process.
- $\Delta G <$  ☐ 0 for a spontaneous process.

[Solution](#)

- 3.54.** Calculate the entropy and Gibbs energy changes for the conversion of 1 mol of liquid water at 100 °C and 1 bar pressure into vapor at the same temperature and a pressure of 0.1 bar. Assume ideal behavior. The heat of vaporization of water at 100 °C is 40.6 kJ mol<sup>-1</sup>.

[Solution](#)

- 3.55.** In the bacterium *nitrobacter* the following reaction occurs:



Use the data in Appendix D to calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  for the reaction.

[Solution](#)

### Energy Conversion

- 3.56.** At 100 atm pressure water boils at 312 °C, while at 5 atm it boils at 152 °C. Compare the Carnot efficiencies of 100-atm and 5-atm steam engines, if  $T_c$  is 30 °C.

[Solution](#)

- 3.57.** A cooling system is designed to maintain a refrigerator at -4 °C in a room at 20 °C. If 10<sup>4</sup> J of heat leaks into the refrigerator each minute, and the system works at 40% of its maximum thermodynamic efficiency, what is the power requirement in watts? [1 watt (W) = 1 J s<sup>-1</sup>.]

[Solution](#)

- 3.58.** A heat pump is employed to maintain the temperature of a house at 25 °C. Calculate the maximum performance factor of the pump when the external temperature is (a) 20 °C, (b) 0 °C, and (c) -20 °C.

[Solution](#)



- 3.59.** A typical automobile engine works with a cylinder temperature of 2000 °C and an exit temperature of 800 °C. A typical octane fuel (molar mass = 114.2 g mol<sup>-1</sup>) has an enthalpy of combustion of -5500 kJ mol<sup>-1</sup> and 1 dm<sup>3</sup> (0.264 U.S. gal) has a mass of 0.80 kg. Calculate the maximum amount of work that could be performed by the combustion of 10 dm<sup>3</sup> of the fuel.

[Solution](#)

- 3.60.** The temperature of a building is maintained at 20 °C by means of a heat pump, and on a particular day the external temperature is 10 °C. The work is supplied to the heat pump by a heat engine that burns fuel at 1000 °C and operates at 20 °C. Calculate the performance factor for the system (i.e., the ratio of the heat delivered to the building to the heat produced by the fuel in the heat engine). Assume perfect efficiencies of the pump and the engine.

[Solution](#)

- 3.61.** Suppose that a refrigerator cools to 0 °C, discharges heat at 25 °C, and operates with 40% efficiency.  
**a.** How much work would be required to freeze 1 kg of water ( $\Delta_f H = -6.02$  kJ mol<sup>-1</sup>)?  
**b.** How much heat would be discharged during the process?

[Solution](#)

### Thermodynamic Relationships

- 3.62.** Show that (a)  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - \kappa P}{\kappa}$ , and (b)  $\left(\frac{\partial U}{\partial P}\right)_T = V(\kappa P - \alpha T)$ , where  $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ , is called the isothermal compressibility coefficient.

$$\left[ \text{Use the relationship } \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \right]$$

[Solution](#)

- 3.63.** Derive an equation of state from

$$dH = T dS + V dP$$

by taking the partial derivative with respect to  $P$  at constant temperature. Then use the appropriate Maxwell relation and the definition of  $\alpha$  to express the partial in terms of easily measured quantities.

[Solution](#)

**3.64.** Derive expressions for (a)  $\alpha$  and (b)  $\kappa$  for an ideal gas.

[Solution](#)

**\*3.65.** Suppose that a gas obeys the van der Waals equation

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Prove that:

$$\left(\frac{\partial U}{\partial V_m}\right)_T = \frac{a}{V_m^2}$$

[Solution](#)

**\*3.66.** Obtain an expression for the Joule-Thomson coefficient for a gas obeying the equation of state:

$$P(V_m - b) = RT$$

in terms of  $R$ ,  $T$ ,  $P$ ,  $V_m$ , and  $C_{P,m}$ .

[Solution](#)

**\*3.67.** Derive the following equations:

a.  $C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)$

b.  $\left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P$

[Solution](#)

**\*3.68.** Starting with the definition of the Helmholtz energy,  $A = U - TS$ , prove that the change in Helmholtz energy for a process at constant temperature is the total work ( $PV$  and non- $PV$ ). (This relationship holds without any restriction as to volume or pressure changes.)

[Solution](#)



**\*3.69.** Prove that if a gas obeys Boyle's law and if in addition  $(\partial U/\partial V)_T = 0$ , it must obey the equation of state  $PV = \text{constant} \times T$ .

[Solution](#)

**\*3.70.** Derive the relationship

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

and confirm that it applies to an ideal gas.

[Solution](#)

**3.71.** Starting from Eq. 3.160,

**a.** Show that  $\ln\left(\frac{f_2}{P_2}\right) = \int_{P_1}^{P_2} \left(\frac{Z-1}{P}\right) dP$ , where  $Z = \frac{PV_m}{RT}$ .

**b.** For a nonideal gas, the equation of state is given as  $PV_m = RT + (b - A/RT^{2/3})P$  (see Example 1.6, p. 42). Derive an expression to find the fugacity of the gas at a given temperature and pressure when the constants  $b$  and  $A$  are given.

[Solution](#)

**3.72.** The van der Waals constants for methane in older units are  $a = 2.283 \text{ L}^2 \text{ bar mol}^{-2}$  and  $b = 0.0428 \text{ L mol}^{-1}$ . Expressing the compression factor as (see Problem 1.52 in Chapter 1):

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT}\right) P + \left(\frac{b}{RT}\right)^2 P^2,$$

Find the fugacity of methane at 500 bar and 298 K.

[Solution](#)

**Essay Questions**

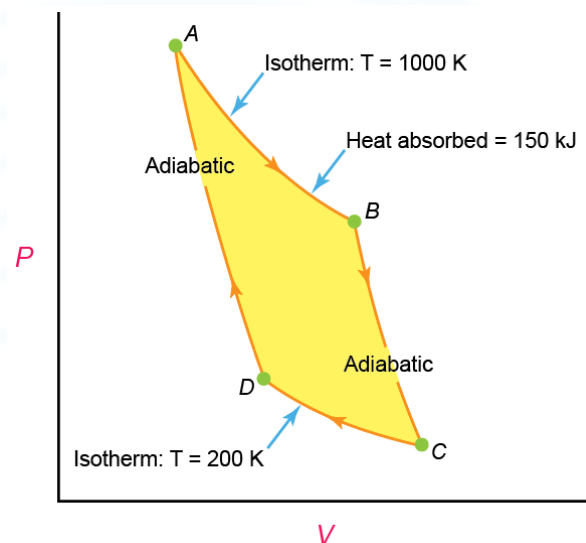
- 3.73.** The frying of a hen's egg is a spontaneous reaction and has a negative Gibbs energy change. The process can apparently be reversed by feeding the fried egg to a hen and waiting for it to lay another egg. Does this constitute a violation of the second law? Discuss.<sup>10</sup>
- 3.74.** Consider the following statements:  
**a.** In a reversible process there is no change in the entropy.  
**b.** In a reversible process the entropy change is  $dq_{\text{rev}}/T$ . How must these statements be qualified so that they are correct and not contradictory?
- 3.75.** Consider the following statements:  
**a.** The solution of certain salts in water involves a decrease in entropy.  
**b.** For any process to occur spontaneously there must be an increase in entropy.  
Qualify these statements so that they are correct and not contradictory, and suggest a molecular explanation for the behavior.
- 3.76.** A phase transition, such as the melting of a solid, can occur reversibly and, therefore,  $\Delta S = 0$ . But it is often stated that melting involves an entropy increase. Reconcile these two statements.

---

<sup>10</sup>In answering this question, a student commented that a hen would never eat a fried egg. We suspect she would if she were hungry and had no alternative. In any case, let us postulate a hen sufficiently eccentric to eat a fried egg.

**Solutions**

3.1. The accompanying diagram represents a reversible Carnot cycle for an ideal gas:



- What is the thermodynamic efficiency of the engine?
- How much heat is rejected at the lower temperature,  $200\text{ K}$ , during the isothermal compression?
- What is the entropy increase during the isothermal expansion at  $1000\text{ K}$ ?
- What is the entropy decrease during the isothermal compression at  $200\text{ K}$ ?
- What is the overall entropy change for the entire cycle?
- What is the increase in Gibbs energy during the process  $A \rightarrow B$ ?

**Solution:**

Given: Carnot Cycle Diagram for Ideal Gas

Required: see above

a) The efficiency for an engine is given by Eq. 3.21 which states that:

$$e = \frac{w}{q_h} = \frac{\cancel{R}(T_h - T_c) \ln\left(\frac{\cancel{V_2}}{\cancel{V_1}}\right)}{\cancel{R}T_h \ln\left(\frac{\cancel{V_2}}{\cancel{V_1}}\right)}$$

$$e = \frac{(T_h - T_c)}{T_h}$$

$$e = \frac{1000 - 200}{1000} = 0.8$$

$$e = 80\%$$

b) We can determine the amount of heat rejected at the lower temperature by making use of Eq. 3.23 which is that of a reversible engine.

$$e = \frac{q_h + q_c}{q_h} \text{ and therefore,}$$

$$\frac{T_h - T_c}{T_h} = \frac{q_h + q_c}{q_h} \rightarrow -\frac{T_h}{T_c} = \frac{q_h}{q_c}$$

$$-q_c = q_h \left( \frac{T_c}{T_h} \right)$$

$$-q_c = 150 \text{ kJ} \times \frac{200 \cancel{\text{K}}}{1000 \cancel{\text{K}}}$$

$$\boxed{\text{heat rejected} = 30 \text{ kJ}}$$

c) The increase in entropy for the system throughout this process can be defined by Eq. 3.55 which gives,

$$\Delta S = \frac{dq_{\text{rev}}}{T}$$

$$S_{\text{inc}} = \frac{q_h}{T_h}$$

$$S_{\text{inc}} = \frac{150\,000 \text{ J}}{1000 \text{ K}}$$

$$\boxed{S_{\text{inc}} = 150 \text{ J K}^{-1}}$$

**d)** We may use the same expression given in part C in order to determine the entropy decrease.

$$\Delta S = \frac{dq_{\text{rev}}}{T}$$

$$S_{\text{decr}} = \frac{q_c}{T_c}$$

$$S_{\text{decr}} = \frac{30\,000 \text{ J}}{200 \text{ K}}$$

$$\boxed{S_{\text{decr}} = 150 \text{ J K}^{-1}}$$

**e)** We must simply take the difference between the entropies calculated in parts C and D.

$$\Delta S = S_{\text{inc}} - S_{\text{decr}}$$

$$\Delta S = (150 - 150) \text{ J K}^{-1}$$

$$\boxed{\Delta S = 0}$$

**f)** Using the well known equation for the Gibbs Free Energy:

$$\Delta S = 150 \text{ J K}^{-1} \text{ and } \Delta H = 0$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 0 - (1000 \text{ K})(150 \text{ J K}^{-1})$$

$$\Delta G = -150\,000 \text{ J}$$

$$\boxed{\Delta G = -150 \text{ kJ}}$$

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**3.2.** An engine operates between 125 °C and 40 °C. What is the minimum amount of heat that must be withdrawn from the reservoir to obtain 1500 J of work?

**Solution:**

Given:  $T_1 = 40\text{ °C}$ ,  $T_2 = 125\text{ °C}$ ,  $w = 1500\text{ J}$

Required:  $q_{\min}$

For this problem, we should start by determining the efficiency of the engine. Efficiency is given by Eq. 3.20:

$$e = \frac{w}{q_h} = \frac{T_h - T_c}{T_h}$$

$$e = \frac{[(125 + 273.15) - (40 + 273.15)]\text{ K}}{(125 + 273.15)\text{ K}}$$

$$e = \frac{(398.15 - 313.15)\text{ K}}{398.15\text{ K}}$$

$$e = 0.213\,487\,379$$

Now that we have the efficiency we will be able to determine the minimum amount of heat that must be withdrawn from the reservoir to obtain 1500 J of work.

$$e = \frac{w}{q_{\min}}$$

$$0.213\,487\,379 = \frac{1500\text{ J}}{q_{\min}}$$

$$q_{\min} = \frac{1500\text{ J}}{0.213\,487\,379}$$

$$q_{\min} = 7026.176\,471\text{ J}$$

$q_{\min} = 7.03\text{ kJ}$

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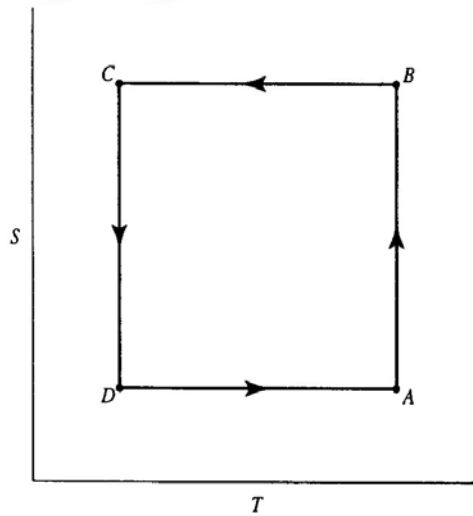
- 3.3.** a. Figure 3.2 shows a Carnot cycle in the form of a pressure-volume diagram. Sketch the corresponding entropy-temperature diagram, labeling the individual steps  $A \rightarrow B$  (isotherm at  $T_h$ ),  $B \rightarrow C$  (adiabatic),  $C \rightarrow D$  (isotherm at  $T_c$ ), and  $D \rightarrow A$  (adiabatic).  
 b. Suppose that a reversible Carnot engine operates between 300 K and a higher temperature  $T_h$ . If the engine produces 10 kJ of work per cycle and the entropy change in the isothermal expansion at  $T_h$  is  $100 \text{ J K}^{-1}$ , what are  $q_h$ ,  $q_c$ , and  $T_h$ ?

**Solution:**

Given: Figure 3.2,  $T_1 = 300 \text{ K}$ ,  $T_2 = T_h$ ,  $w = 10 \text{ kJ}$ ,  $\Delta S = 100 \text{ J K}^{-1}$

Required:  $q_h$ ,  $q_c$ , and  $T_h$   $S$ - $T$  diagram

a)



b) From Eq. 3.23 we are given,



$$\frac{T_h - T_c}{T_h} = \frac{q_h - q_c}{q_h} \text{ or } -\frac{T_h}{T_c} = \frac{q_h}{q_c}$$

$$\frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

$$\frac{q_h}{T_h} + \frac{q_c}{300 \text{ K}} = 0$$

We know that the work performed *by* the system is equal to:

$$-w = q_h + q_c = 10 \text{ kJ}$$

We can determine the change in entropy which will then enable us to find  $q_c$  and  $q_h$ .

$$-w = q_h + q_c = 10 \text{ kJ}$$

$$\Delta S = \frac{q}{T} \text{ thus, } \Delta S_h = \frac{q_h}{T_h}$$

$$\Delta S_h = \frac{q_h}{T_h} = 100 \text{ J K}^{-1}$$

$$100 \text{ J K}^{-1} + \frac{q_c}{300 \text{ K}} = 0$$

$$\frac{q_c}{300 \text{ K}} = -100 \text{ J K}^{-1}$$

$$q_c = -30\,000 \text{ J}$$

$$\boxed{q_c = -30 \text{ kJ}}$$

$$q_h + q_c = 10 \text{ kJ} \rightarrow q_h = 10 \text{ kJ} - (-30 \text{ kJ})$$

$$\boxed{q_h = 40 \text{ kJ}}$$

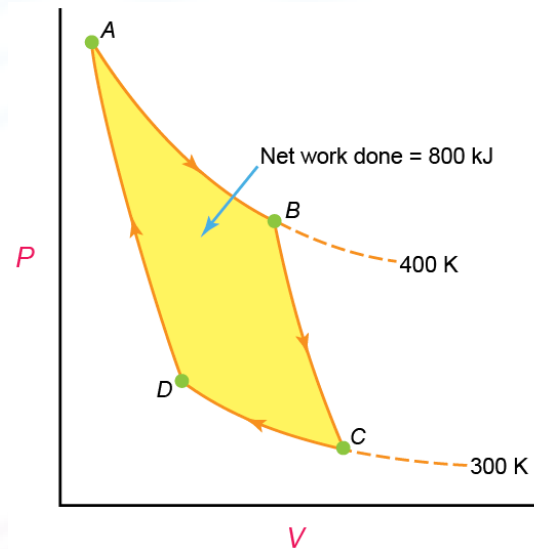
$$T_h = -T_c \frac{q_h}{q_c} = (-300 \text{ K}) \frac{40 \text{ kJ}}{-30 \text{ kJ}}$$

$$\boxed{T_h = 400 \text{ K}}$$

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- 3.4. The following diagram represents a reversible Carnot cycle for an ideal gas:
- What is the thermodynamic efficiency of the engine?
  - How much heat is absorbed at 400 K?
  - How much heat is rejected at 300 K?
  - What is the entropy change in the process  $A \rightarrow B$ ?
  - What is the entropy change in the entire cycle?
  - What is the Gibbs energy change in the process  $A \rightarrow B$ ?
  - In order for the engine to perform 2 kJ of work, how much heat must be absorbed?



**Solution:**

Given: Carnot Cycle for Ideal Gas

Required: see above

a) According to Eq. 3.21:

$$e = \frac{T_h - T_c}{T_h}$$

$$e = \frac{(400 - 300) \text{ K}}{400 \text{ K}}$$

$$e = 0.25$$

$$\boxed{e = 25\%}$$

**b)** The heat absorbed can also be found using a rearrangement of the previously given equation.

$$e = \frac{T_h - T_c}{T_h} = \frac{w}{q_h}$$

$$q_h (400 \text{ K}) = \frac{w}{e} = \frac{800 \text{ J}}{0.25}$$

$$q_h (400 \text{ K}) = 3200 \text{ J}$$

$$\boxed{q_h (400 \text{ K}) = 3.2 \text{ kJ}}$$

**c)** The heat rejected can be found by the following:

$$q_{\text{rejected}} = q_h - q_c$$

$$q_{\text{rejected}} = 3200 \text{ J} - 800 \text{ J}$$

$$q_{\text{rejected}} = 2400 \text{ J}$$

$$\boxed{q_{\text{rejected}} = 2.4 \text{ kJ}}$$

**d)** The entropy change from A  $\rightarrow$  B can be determined by:

$$\Delta S_{A \rightarrow B} = \frac{q_h}{T_h}$$

$$\Delta S_{A \rightarrow B} = \frac{3200 \text{ J}}{400 \text{ K}}$$

$$\boxed{\Delta S_{A \rightarrow B} = 8 \text{ J K}^{-1}}$$

e) We can say that  $\Delta S_{A \rightarrow B}^{(1)}$  denotes the change in entropy in going from A to B by path 1. Conversely,  $\Delta S_{B \rightarrow A}^{(2)}$  denotes the change in entropy in going from B to A along path 2. The change in entropy of the second case/path is identical in magnitude but opposite in sign to the entropy change in the first case/path. This would mean that,

$$\Delta S_{B \rightarrow A}^{(2)} = -\Delta S_{A \rightarrow B}^{(1)} \text{ which is given by Eq. 3.35.}$$

The total change in entropy for the system is therefore,

$$\boxed{\Delta S = 0}$$

f) Since we know that  $\Delta H = 0$ , we can therefore use the equation that describes the Gibbs Free Energy in order to find the answer.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 0 - (400 \text{ K})(8.0 \text{ J K}^{-1})$$

$$\Delta G = -3200 \text{ J}$$

$$\boxed{\Delta G = -3.2 \text{ kJ}}$$

g) We can use the expression which defines the efficiency calculated in the first part of this question in order to determine the amount of heat which must be absorbed.

$$e = \frac{T_h - T_c}{T_h} = \frac{w}{q_h}$$

$$q_h = \frac{w}{e}$$

$$q_h = \frac{2000 \text{ J}}{0.25}$$

$$q_h = 8000 \text{ J}$$

$$\boxed{q_h = 8.0 \text{ kJ}}$$

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- 3.5.** Suppose that an iceberg weighing  $10^9$  kg were to drift into a part of the ocean where the temperature is  $20^\circ\text{C}$ . What is the maximum amount of work that could be generated while the iceberg is melting? Assume the temperature of the iceberg to be  $0^\circ\text{C}$ . The latent heat of fusion of ice is  $6.025\text{ kJ mol}^{-1}$ .]]  
If the process occurred in one day, what would be the power produced?

**Solution:**

Given: Iceberg:  $m_{\text{iceberg}} = 10^9\text{ kg}$ ,  $T_{\text{ocean}} = 20^\circ\text{C} = 293.15\text{ K}$ ,  $T_{\text{iceberg}} = 0^\circ\text{C}$ ,  $\Delta_f H_{\text{ice}} = 6.025\text{ kJ mol}^{-1}$

Required:  $w_{\text{max}}$ ,  $P(1\text{ day})$

The heat that is transferred from the water to the melting iceberg is given by;

$$q = \frac{m}{M} \Delta H_{\text{fusion}}$$

$$q = \frac{10^{12}\text{ g}}{18\text{ g mol}^{-1}} (6.025\text{ kJ mol}^{-1})$$

$$q = 3.347\ 222\ 222 \times 10^{11}\text{ kJ}$$

The fraction of this that can be converted into work can be determined by Eq. 3.21;

$$e = \frac{T_h - T_c}{T_h}$$

$$e = \frac{[(20 + 273.15) - (0 + 273.15)]\text{ K}}{(20 + 273.15)\text{ K}}$$

$$e = \frac{(293.15 - 273.15)\text{ K}}{293.15\text{ K}}$$

$$e = 0.068\ 224\ 458$$

Using a different version of Eq. 2.21 we can not determine the amount of work available.

$$e = \frac{w}{q_h}$$

$$w = eq_h$$

$$w = (0.068\,224\,458)(3.347\,222\,222 \times 10^{11} \text{ kJ})$$

$$w = 2.283\,624\,219 \times 10^{10} \text{ kJ}$$

$$\boxed{w = 2.284 \times 10^{10} \text{ kJ}}$$

Power is simply defined as the amount of work done in a unit time. This can be easily found for a single day.

$$\frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hour}} \times \frac{24 \text{ hrs}}{1 \text{ day}}$$

$$t = 86\,400 \text{ s}$$

$$P = \frac{w}{t}$$

$$P = \frac{2.283\,624\,219 \times 10^{10} \text{ kJ}}{86\,400 \text{ s}}$$

$$P = 264\,308.3587 \text{ kJ s}^{-1}$$

$$\boxed{P = 2.643 \times 10^5 \text{ kJ s}^{-1}}$$

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**3.6.** Show that the change in the internal energy of an ideal gas during an isothermal expansion is zero, i.e.,  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ .

Compare this result to Eq. 3.148 for a van der Waals gas.

**Solution:**

Given:  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ .

Required: prove it

Let us use the thermodynamic equation of state given by Eq. 3.128 which states that:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

From the Ideal Gas Law, we know that  $PV = nRT$  which can be slightly altered to get:

$$P = \frac{nRT}{V}$$

$$P = \frac{RT}{V_m}$$

Now taking the partial derivative of this expression with respect to temperature and keeping volume constant,

$$P = \frac{RT}{V_m}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m}$$

This can now be substituted into Eq. 3.128 to obtain,

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{R}{V_m}\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + \left(\frac{RT}{V_m}\right) \rightarrow \left(\frac{\partial U}{\partial V}\right)_T = -P + P \rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$$

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**3.7.** Calculate the entropies of vaporization in  $\text{J K}^{-1} \text{mol}^{-1}$  of the following substances, from their boiling points and enthalpies of vaporization:

	Boiling Point/K	$\Delta_{\text{vap}}H/\text{kJ mol}^{-1}$
$\text{C}_6\text{H}_6$	353	30.8
$\text{CHCl}_3$	334	29.4
$\text{H}_2\text{O}$	373	40.6
$\text{C}_2\text{H}_5\text{OH}$	351	38.5

In terms of the structures of the liquids, suggest reasons for the higher values observed for  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_5\text{OH}$ .

**Solution:**

Given: see table above

Required:  $\Delta_{\text{vap}}S$  for all species in the above table

It is possible to heat a solid sufficiently slowly at its melting point such that the equilibrium between the liquid and solid phases is hardly disturbed. This means that the process is reversible (ie. it follows a path of successive equilibrium states) and the latent heat of melting is also reversible.

The entropy of melting (ie. fusion) is given by Eq. 3.49:

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}}$$

Given the data in the table above, we obtain:

**Benzene:**

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}}$$

$$\Delta_{\text{fus}} S = \frac{30.8 \text{ kJ mol}^{-1}}{353 \text{ K}}$$

$$\Delta_{\text{fus}} S = \frac{30\,800 \text{ J mol}^{-1}}{353 \text{ K}}$$

$$\boxed{\Delta_{\text{fus}} S = 87.3 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**Trichloromethane:**

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}}$$

$$\Delta_{\text{fus}} S = \frac{29.4 \text{ kJ mol}^{-1}}{334 \text{ K}}$$

$$\Delta_{\text{fus}} S = \frac{29\,400 \text{ J mol}^{-1}}{334 \text{ K}}$$

$$\boxed{\Delta_{\text{fus}} S = 88.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**Water:**

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}}$$

$$\Delta_{\text{fus}} S = \frac{40.6 \text{ kJ mol}^{-1}}{373 \text{ K}}$$

$$\Delta_{\text{fus}} S = \frac{40\,600 \text{ J mol}^{-1}}{373 \text{ K}}$$

$$\boxed{\Delta_{\text{fus}} S = 109 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**Ethanol:**

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}}$$

$$\Delta_{\text{fus}}S = \frac{38.5 \text{ kJ mol}^{-1}}{351 \text{ K}}$$

$$\Delta_{\text{fus}}S = \frac{38\,500 \text{ J mol}^{-1}}{351 \text{ K}}$$

$$\boxed{\Delta_{\text{fus}}S = 110 \text{ J K}^{-1} \text{ mol}^{-1}}$$

A higher value for entropy is correlated to the nature of the hydrogen bonding in the latter two species.

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**3.8.** Calculate the standard entropies of formation of (a) liquid methanol and (b) solid urea, making use of the absolute entropies listed in Table 3.2 (p. 120).

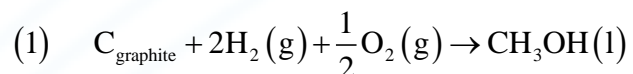
**Solution:**

Given: Table 3.2

Required:  $\Delta_f S^\circ$  for methanol and urea

We have to first write down the complete and balanced equations required for the individual equation. We have seen in previous chapters that,

**a)** For liquid methanol:



According to Eq. 3.69 and Table 3.2;

$$\Delta_f S^\circ = \sum \Delta_f S^\circ (\text{products}) - \sum \Delta_f S^\circ (\text{reactants})$$

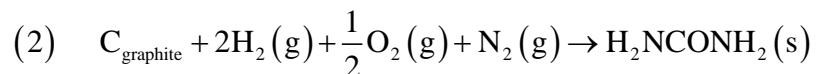
$$\Delta_f S^\circ = \Delta_f S^\circ (\text{CH}_3\text{OH}, \text{l}) - \left( 2\Delta_f S^\circ (\text{H}_2, \text{g}) + \frac{1}{2}\Delta_f S^\circ (\text{O}_2, \text{g}) + \Delta_f S^\circ (\text{C}_{\text{graphite}}) \right)$$

$$\Delta_f S^\circ = \Delta_f S^\circ (\text{CH}_3\text{OH}, \text{l}) - 2\Delta_f S^\circ (\text{H}_2, \text{g}) - \frac{1}{2}\Delta_f S^\circ (\text{O}_2, \text{g}) - \Delta_f S^\circ (\text{C}_{\text{graphite}})$$

$$\Delta_f S^\circ = \left[ 126.80 - (2 \times 130.68) - \left( \frac{1}{2} \times 205.14 \right) - (5.74) \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta_f S^\circ = -242.87 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**b)** For the formation of solid urea:



According to Eq. 3.69 and Table 3.2;

$$\Delta_f S^\circ = \sum \Delta_f S^\circ (\text{products}) - \sum \Delta_f S^\circ (\text{reactants})$$

$$\Delta_f S^\circ = \Delta_f S^\circ (\text{H}_2\text{NCONH}_2, \text{s}) - \left( \Delta_f S^\circ (\text{N}_2, \text{g}) + \frac{1}{2} \Delta_f S^\circ (\text{O}_2, \text{g}) + 2\Delta_f S^\circ (\text{H}_2, \text{g}) + \Delta_f S^\circ (\text{C}_{\text{graphite}}) \right)$$

$$\Delta_f S^\circ = \Delta_f S^\circ (\text{H}_2\text{NCONH}_2, \text{s}) - \Delta_f S^\circ (\text{N}_2, \text{g}) - \frac{1}{2} \Delta_f S^\circ (\text{O}_2, \text{g}) - 2\Delta_f S^\circ (\text{H}_2, \text{g}) - \Delta_f S^\circ (\text{C}_{\text{graphite}})$$

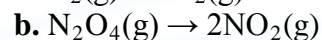
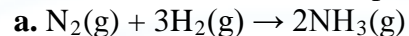
$$\Delta_f S^\circ = \left[ 104.60 - (191.61) - \left( \frac{1}{2} \times 205.14 \right) - (2 \times 130.68) - (5.74) \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta_f S^\circ = -456.68 \text{ J K}^{-1} \text{ mol}^{-1}}$$

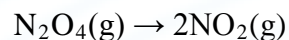
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**3.9.** Calculate the standard entropies for the following reactions at 25 °C:

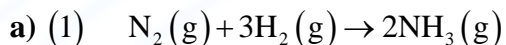


**Solution:**



Required:  $\Delta S^\circ$  for both reactions

We will first write the balanced equations for each reaction. Then apply Eq. 3.69 in order to determine the standard entropy changes for both A and B.



Using Eq. 3.69 together with data from Table 3.2 we obtain,

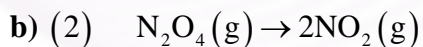
$$\Delta S^\circ = \sum \Delta S^\circ (\text{products}) - \sum \Delta S^\circ (\text{reactants})$$

$$\Delta S^\circ = 2\Delta S^\circ (\text{NH}_3, \text{g}) - (3\Delta S^\circ (\text{H}_2, \text{g}) + \Delta S^\circ (\text{N}_2, \text{g}))$$

$$\Delta S^\circ = 2\Delta S^\circ (\text{NH}_3, \text{g}) - 3\Delta S^\circ (\text{H}_2, \text{g}) - \Delta S^\circ (\text{N}_2, \text{g})$$

$$\Delta S^\circ = [(2 \times 192.45) - (3 \times 130.68) - (191.61)] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ = -198.75 \text{ J K}^{-1} \text{ mol}^{-1}}$$



Using Eq. 3.69 together with data from Appendix D we obtain,

$$\Delta S^\circ = \sum \Delta S^\circ (\text{products}) - \sum \Delta S^\circ (\text{reactants})$$

$$\Delta S^\circ = 2\Delta S^\circ (\text{NO}_2, \text{g}) - \Delta S^\circ (\text{N}_2\text{O}_4, \text{g})$$

$$\Delta S^\circ = (2 \times 240.1 - 304.2) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ = 176 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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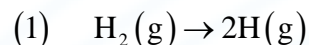
**3.10.** Calculate the standard entropy for the dissociation of  $\text{H}_2(\text{g})$  into atomic hydrogen  $2[\text{H}(\text{g})]$  at 298.15 K and 1273.15 K.  
 $C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1}$  :  $\text{H}_2(\text{g})$ , 28.824;  $\text{H}(\text{g})$ , 20.784.

**Solution:**

Given: dissociation of Hydrogen:  $T_1 = 298.15 \text{ K}$   $T_2 = 1273.15 \text{ K}$ ,  $C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1}$  :  $\text{H}_2(\text{g})$ , 28.824;  $\text{H}(\text{g})$ , 20.784

Required:  $\Delta_r S^\circ$

As in the last few problems, we will first write the balanced equation for the reaction.



First, it is important that we determine the entropy change at the initial temperature for the dissociation of hydrogen gas. Using this value, we can calculate the *increase* in entropy for the overall increase in temperature (ie. to 1273.15K ). Assuming that the heat capacity is constant throughout this temperature range and using the data given in Appendix D;

$$\Delta S^\circ = \sum \Delta S^\circ (\text{products}) - \sum \Delta S^\circ (\text{reactants})$$

$$\Delta S^\circ = 2\Delta S^\circ (\text{H}, \text{g}) - \Delta S^\circ (\text{H}_2, \text{g})$$

$$\Delta S^\circ = \left[ (2 \times 114.717) - (130.680) \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S^\circ = 98.754 \text{ J K}^{-1} \text{ mol}^{-1}$$

Beginning with Eq. 3.55, it can be integrated to yield:

$$dS = \frac{dq_{\text{rev}}}{T} = nC_{V,m} \frac{dT}{T} + nR \frac{dV}{V}$$

$$\Delta S = S_2 - S_1 = n \int_{T_1}^{T_2} C_{V,m} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

However, we are working under constant *pressure*, not constant volume so we need formulate an expression in terms of  $C_{P,m}$ . When the heat capacity is independent of temperature, we may further simplify to:



$$\Delta S = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

An easier way to do this is to take Eq. 2.50 (Chapter 2) and instead of writing it in terms of enthalpy, we switch the units to entropy of dissociation. This substitution leads to determine the entropy changes at different temperatures providing that the first has already been found.

$$\Delta H_m(T_2) - \Delta H_m(T_1) = \int_{T_1}^{T_2} \Delta C_p dT$$

$$\Delta_r S^\circ(T_2) - \Delta_r S^\circ(T_1) = \int_{T_1}^{T_2} \frac{\Delta_r C_p^\circ}{T} dT$$

$$\Delta_r S^\circ(1273.15 \text{ K}) = \Delta_r S^\circ(298.15 \text{ K}) + \int_{T_1}^{T_2} \frac{\Delta_r C_p^\circ}{T} dT$$

Where,  $\Delta_r C_p^\circ = \sum_i \nu_i C_{p,i}^\circ$  for the reaction. Again, the heat capacity is independent of temperature therefore;

$$\Delta_r S^\circ(1273.15 \text{ K}) = \Delta_r S^\circ(298.15 \text{ K}) + \sum_i \nu_i C_{p,i}^\circ \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta_r S^\circ(1273.15 \text{ K}) = (98.754 \text{ J K}^{-1} \text{ mol}^{-1}) + [(2 \times 20.784 - 28.824) \text{ J K}^{-1} \text{ mol}^{-1}] \ln \frac{1273.15}{298.15}$$

$$\Delta_r S^\circ(1273.15 \text{ K}) = \left[ 98.754 + 12.744 \ln \frac{1273.15}{298.15} \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S^\circ(1273.15 \text{ K}) = [98.754 + 18.499 \ 862] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta_r S^\circ(1273.15 \text{ K}) = 117.25 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.11.** One mole of an ideal gas, with  $C_{V,m} = \frac{3}{2}R$ , is heated (a) at constant pressure and (b) at constant volume, from 298 K to 353 K. Calculate  $\Delta S$  for the system in each case.

**Solution:**

Given: Ideal Gas:  $n = 1$  mol,  $C_{V,m} = \frac{3}{2}R$ ,  $T_1 = 298$  K,  $T_2 = 353$  K

Required:  $\Delta S_m$  in each case

**a)** For one mole of Ideal Gas at *constant pressure* and using Eq. 3.55:

$$dS = \frac{dq_{\text{rev}}}{T} = nC_{V,m} \frac{dT}{T} + nR \frac{dV}{V}$$

It can then be integrated to yield,

$$dS = \frac{dq_{\text{rev}}}{T} = nC_{V,m} \frac{dT}{T} + nR \frac{dV}{V}$$

$$\Delta S = S_2 - S_1 = n \int_{T_1}^{T_2} C_{V,m} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

Since we are working at constant pressure, we will find that;

$$\Delta S = n \int_{T_1}^{T_2} C_{V,m} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S_m = \int_{T_1}^{T_2} \frac{C_{V,m}}{T} dT \text{ or } \Delta S_m = \int_{T_1}^{T_2} \frac{C_{P,m}}{T} dT$$

$$\text{given that } C_{V,m} = \frac{3}{2}R \text{ and } C_{P,m} - C_{V,m} = R;$$

$$C_{V,m} = C_{P,m} - R \rightarrow C_{P,m} = R + \frac{3}{2}R = \frac{5}{2}R$$

$$\Delta S_m = \int_{T_1}^{T_2} \frac{C_{P,m}}{T} dT$$

$$\Delta S_m = C_{P,m} \ln T \Big|_{298}^{353}$$

$$\Delta S_m = \frac{5}{2}R \ln \frac{353}{298}$$

$$\boxed{\Delta S_m = 3.52 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**b)** Using the same method for one mole of Ideal Gas at *constant volume*:

$$\Delta S_m = \int_{T_1}^{T_2} \frac{C_{V,m}}{T} dT$$

$$\text{given that } C_{V,m} = \frac{3}{2}R$$

$$\Delta S_m = C_{V,m} \ln T \Big|_{298}^{353}$$

$$\Delta S_m = \frac{3}{2}R \ln \frac{353}{298}$$

$$\boxed{\Delta S_m = 2.11 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.12.** One mole each of  $\text{N}_2$  and  $\text{O}_2$  and  $\frac{1}{2}$  mol of  $\text{H}_2$ , at  $25^\circ\text{C}$  and 1 atm pressure, are mixed isothermally; the final total pressure is 1 atm. Calculate  $\Delta S$ , on the assumption of ideal behavior.

**Solution:**

Given:  $n_{\text{H}_2} = \frac{1}{2}$  mol,  $n_{\text{N}_2} = 1$  mol,  $n_{\text{O}_2} = 1$  mol,  $T = 25^\circ\text{C}$ ,  $P = 1$  atm,  $P_{\text{tot}} = 1$  atm

Required:  $\Delta S_{\text{MIX}} = -R \sum_i x_i \ln x_i$

Total number of moles:  $1+1+0.5 = 2.5$

Mole fractions are

$$n_{\text{H}_2} = \frac{0.5}{2.5}; n_{\text{N}_2} = \frac{1}{2.5}; n_{\text{O}_2} = \frac{1}{2.5};$$

$$\Delta S_{\text{MIX}} = -R \sum_i x_i \ln x_i = -R \left[ \frac{1}{5} \ln \frac{1}{5} + \frac{2}{5} \ln \frac{2}{5} + \frac{2}{5} \ln \frac{2}{5} \right]$$

$$\Delta S_{\text{MIX}} = -8.314 [-0.3219 - 0.3665 - 0.3665] = 8.77 \text{ e.u.}$$

This is the molar entropy of mixing. For 2.5 moles,

$$\Delta S_{\text{MIX}} = 8.77 \text{ e.u.} \times 2.5 \text{ moles} = 21.93 \text{ J K}^{-1}$$

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**3.13.** Initially 1 mol of  $O_2$  is contained in a 1-liter vessel, and 5 mol of  $N_2$  are in a 2-liter vessel; the two vessels are connected by a tube with a stopcock. If the stopcock is opened and the gases mix, what is the entropy change?

**Solution:**

Given:  $n_{O_2} = 1$  mol,  $V_{O_2} = 1$  litre,  $n_{N_2} = 5$  mol,  $V_{N_2} = 2$  litre

Required:  $\Delta S_{\text{mix}}$

In this instance we will assume that both the oxygen and nitrogen behave ideally and are initially at equal pressure. When we allow the gases to mix reversibly, the volume will eventually come to equilibrium and we will be able to determine the entropy changes for either species according to Eq. 3.58 and Eq. 3.59:

$$(1) \Delta S_{O_2} = n_{O_2} R \ln \frac{V_{O_2} + V_{N_2}}{V_{O_2}}$$

$$\Delta S_{O_2} = (1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{(1+2) \cancel{\text{L}}}{1 \cancel{\text{L}}}$$

$$\Delta S_{O_2} = 9.134 \ 411 \ 874 \text{ J K}^{-1}$$

$$(1) \Delta S_{N_2} = n_{N_2} R \ln \frac{V_{N_2} + V_{O_2}}{V_{N_2}}$$

$$\Delta S_{N_2} = (5.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{(2+1) \cancel{\text{L}}}{2 \cancel{\text{L}}}$$

$$\Delta S_{N_2} = 16.856 \ 198 \ 21 \text{ J K}^{-1}$$

$$\Delta S = \Delta S_{N_2} + \Delta S_{O_2}$$

$$\Delta S = (16.856 \ 198 \ 21 + 9.134 \ 411 \ 874) \text{ J K}^{-1}$$

$$\Delta S = 25.990 \ 610 \ 08 \text{ J K}^{-1}$$

$$\boxed{\Delta S = 25.99 \text{ J K}^{-1}}$$

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**3.14.** Calculate the entropy of mixing per mole of air, taking the composition by volume to be 79% N<sub>2</sub>, 20% O<sub>2</sub>, and 1% Ar.

**Solution:**

Given: Air: Composition 79% N<sub>2</sub>, 20% O<sub>2</sub>, and 1% Ar

Required:  $\Delta S_{\text{mix}}$  for air

Since we are given the relative approximations for each of the species in air, we can start off by calculating the respective mole fractions. This concept was seen in Chapter 1.

$$x_i = \frac{n_i}{n}$$

Where,  $x_i$  is the mole fraction,  $n_i$  is the number of moles per species and  $n$  is the total number of moles for the system.

**Nitrogen:**

$$x_{\text{N}_2} = \frac{n_{\text{N}_2}}{n}$$

$$x_{\text{N}_2} = \frac{79}{100}$$

$$x_{\text{N}_2} = 0.79$$

**Oxygen:**

$$x_{\text{O}_2} = \frac{n_{\text{O}_2}}{n}$$

$$x_{\text{O}_2} = \frac{20}{100}$$

$$x_{\text{O}_2} = 0.20$$

**Argon:**

$$x_{\text{Ar}} = \frac{n_{\text{Ar}}}{n}$$

$$x_{\text{Ar}} = \frac{1}{100}$$

$$x_{\text{Ar}} = 0.01$$

Since we have seen that  $\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2 + \Delta S_3$  then we can re-write the expression to get Eq. 3.65:

$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$x_1 = \frac{n_1}{n_1 + n_2 + n_3} \dots$$

$$\Delta S_{\text{mix}} = n_1 R \ln \frac{1}{x_1} + n_2 R \ln \frac{1}{x_2} + n_3 R \ln \frac{1}{x_3}$$

$$\Delta S_{\text{mix}} = n_{\text{N}_2} R \ln \frac{1}{x_{\text{N}_2}} + n_{\text{O}_2} R \ln \frac{1}{x_{\text{O}_2}} + n_{\text{Ar}} R \ln \frac{1}{x_{\text{Ar}}}$$

$$\Delta S_{\text{mix}} = -R (x_{\text{N}_2} \ln x_{\text{N}_2} + x_{\text{O}_2} \ln x_{\text{O}_2} + x_{\text{Ar}} \ln x_{\text{Ar}})$$

$$\Delta S_{\text{mix}} = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} [(0.79 \ln 0.79) + (0.20 \ln 0.20) + (0.01 \ln 0.01)]$$

$$\Delta S_{\text{mix}} = 4.607 \text{ 562 72 J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_{\text{mix}} (\text{air}) = 4.61 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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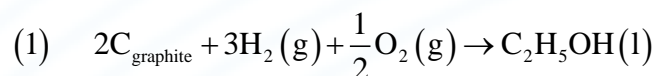
**3.15.** From the data given in Table 3.2 (p. 120), calculate the standard entropy of formation  $\Delta_f S^\circ$  of liquid ethanol at 25 °C.

**Solution:**

Given: Table 3.2

Required:  $\Delta_f S^\circ$  ethanol

Remember that we have already completed this exercise for methanol! This should be a very quick review and makes use of Eq. 3.69. Let us first give the balanced reaction:



Let us use the data given in Table 3.2 to obtain,

$$\Delta_f S^\circ = \sum \Delta S^\circ (\text{products}) - \sum \Delta S^\circ (\text{reactants})$$

$$\Delta_f S^\circ = \Delta S^\circ (\text{C}_2\text{H}_5\text{OH}, \text{l}) - \left[ \frac{1}{2} \Delta S^\circ (\text{O}_2, \text{g}) + 3 \Delta S^\circ (\text{H}_2, \text{g}) + 2 \Delta S^\circ (\text{C}_{\text{graphite}}) \right]$$

$$\Delta_f S^\circ = \left[ 160.70 - \left( \frac{1}{2} \times 205.14 \right) - (3 \times 130.68) - (2 \times 5.74) \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta_f S^\circ (\text{C}_2\text{H}_5\text{OH}) = -345.40 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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- 3.16.** **a.** One mole of an ideal gas at 25 °C is allowed to expand reversibly and isothermally from 1 dm<sup>3</sup> to 10 dm<sup>3</sup>. What is  $\Delta S$  for the gas, and what is  $\Delta S$  for its surroundings?
- b.** The same gas is expanded adiabatically and irreversibly from 1 dm<sup>3</sup> to 10 dm<sup>3</sup> with no work done. What is the final temperature of the gas? What is  $\Delta S$  for the gas, and what is  $\Delta S$  for the surroundings? What is the net  $\Delta S$ ?

**Solution:**

Given: Ideal Gas:  $n = 1 \text{ mol}$ ,  $T = 25 \text{ °C}$ ,  $V_i = 1 \text{ dm}^3$ ,  $V_f = 10 \text{ dm}^3$

Required: see above (there are two different conditions here)

**a)** Ideal Gas undergoing a reversible and isothermal expansion.

Since we are working at constant temperature, Eq. 3.51 will hold true. We will use it to calculate the entropy change for both the gas and the surroundings.

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{gas}} = (1.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{10}{1}$$

$$\Delta S_{\text{gas}} = 19.144 \text{ 844 J K}^{-1}$$

$$\boxed{\Delta S_{\text{gas}} = 19.14 \text{ J K}^{-1}}$$

Let us now consider Eq. 3.70 which gives the condition for equilibrium in such a system.

$$dS^{\text{total}} = dS^{\text{syst}} + dS^{\text{surr}} = 0$$

here,  $dS^{\text{syst}} = dS^{\text{gas}}$  therefore,

$$\Delta S_{\text{tot}} = \Delta S_{\text{gas}} + \Delta S_{\text{surr}} = 0$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{gas}}$$

$$\boxed{\Delta S_{\text{surr}} = -19.14 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**b)** Ideal Gas undergoing an adiabatic, irreversible expansion.

Remember from Chapter 3 that for an adiabatic process,  $\Delta U = 0$ ,  $\Delta H = 0$  (due to their temperature change dependence) and we are told that no work is done. Since we have shown that  $\Delta U = 0$ , we also know that there is no change in temperature throughout the reaction.

$$\Delta U = 0$$

$$\Delta U = mC\Delta T = mC(T_f - T_i)$$

$$\frac{\Delta U}{mC} = 0 \text{ therefore, } \boxed{T_f = T_i = 298.15 \text{ K}}$$

Due to the fact that  $\Delta S_{\text{gas}}$  can only be calculated from the reversible process it would follow:

$$\boxed{\Delta S_{\text{gas}} = 19.14 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{gas}} + \Delta S_{\text{surr}} = 0$$

$$dS^{\text{surr}} = dq_{\text{surr}}^{\text{rev}} = dU_{\text{surr}}^{\text{rev}} = 0$$

$$\boxed{\Delta S_{\text{surr}} = 0}$$

$$\Delta S_{\text{net}} = \Delta S_{\text{gas}} - \Delta S_{\text{surr}}$$

$$\boxed{\Delta S_{\text{net}} = 19.14 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.17.** One mole of liquid water at 0.00 °C and 1 atm pressure is turned into steam at 100.0 °C and 1 atm pressure by the following two paths:

**a.** Heated at constant pressure to 100.0°C, and allowed to boil into steam ( $\Delta_{\text{vap}}H^\circ = 40.67 \text{ J mol}^{-1}$  at this temperature).

**b.** Pressure lowered to 0.006 02 atm so that water evaporates to steam at 0 °C ( $\Delta_{\text{vap}}H^\circ = 44.92 \text{ J mol}^{-1}$  at this temperature), heated at the constant pressure of 0.006 02 atm to 100.0 °C, and compressed at 100.0 °C to 1 atm pressure.

Calculate the entropy change along each path and verify that they are the same, thus proving that  $\Delta S^\circ$  is a state property. The  $C_{P,m}$  for liquid water and water vapor can be found in Table 2.1. [The paths and the enthalpies of vaporization are adapted from Table 6.1, Gordon M. Barrow, *Physical Chemistry*, 5th Ed., New York: McGraw-Hill, 1988.]

**Solution:**

Given: see above, Table 2.1

Required:  $\Delta S^\circ$

Since we are beginning with water at 0.00 °C and 1 atm pressure and we are turning it into steam in the process, we need to consider the entropy changes that occur when moving between states.

**a)** Heated at constant pressure to 100.0°C, and allowed to boil into steam

$$\begin{aligned}\Delta S^\circ(373.15 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) &= \int_{T_i}^{T_f} \frac{C_{P,m(l)}}{T} dT + \frac{\Delta_{\text{vap}}H^\circ}{T} \\ \Delta S^\circ(373.15 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) &= \int_{273.15}^{373.15} \frac{C_{P,m(l)}}{T} dT + \frac{40.67 \text{ J mol}^{-1}}{373.15 \text{ K}} \\ \Delta S^\circ(373.15 \text{ K}) &= 75.48 \text{ J K}^{-1} \text{ mol}^{-1} \ln \frac{373.15 \text{ K}}{273.15 \text{ K}} + 0.108 991 \text{ J K}^{-1} \text{ mol}^{-1} \\ \boxed{\Delta S^\circ(373.15 \text{ K})} &= 23.66 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

**b)** Pressure lowered to 0.006 02 atm so that water evaporates to steam at 0 °C, heated at the constant pressure of 0.006 02 atm to 100.0 °C and compressed at 100.0 °C to 1 atm pressure.

One should recognize that changing the pressure on the surface of a liquid does not affect the entropy of the system. We must therefore consider the entropy changes for the vaporization process (heating the vapor at constant pressure and compressing the vapor at constant temperature).

$$\Delta S^\circ(373.15 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = \frac{\Delta_{\text{vap}} H^\circ}{T} + \int_{T_i}^{T_f} \frac{C_{P,m(\text{g})}}{T} dT + R \ln \frac{V_f}{V_i}$$

$$\Delta S^\circ(373.15 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = \frac{44.92 \text{ J mol}^{-1}}{373.15 \text{ K}} + \int_{273.15}^{373.15} \frac{C_{P,m(\text{g})}}{T} dT + (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{P_1}{P_2}$$

$$C_{P,m(\text{g})} = 30.54 + 10.29 \times 10^{-3} T$$

$$\begin{aligned} \Delta S^\circ(373.15) &= \frac{44.92 \text{ J mol}^{-1}}{373.15 \text{ K}} + \int_{273.15}^{373.15} \frac{30.54 + 10.29 \times 10^{-3} T}{T} dT \\ &\quad + (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{0.00602 \text{ atm}}{1.00 \text{ atm}} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ(373.15) &= 0.120 \ 380 \ 544 \text{ J K}^{-1} \text{ mol}^{-1} + 30.54 \ln \frac{373.15 \text{ K}}{273.15 \text{ K}} \\ &\quad + 10.29 \times 10^{-3} (373.15 - 273.15) \text{ K} + (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 0.00602 \end{aligned}$$

$$\Delta S^\circ(373.15) = (0.120 \ 380 \ 544 + 9.527 \ 239 \ 732 + 1.029 - 42.509 \ 278 \ 25) \text{ J K}^{-1} \text{ mol}^{-1}$$

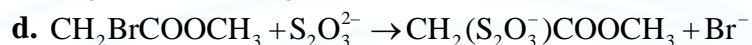
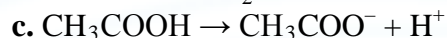
$$\Delta S^\circ(373.15) = -31.832 \ 657 \ 97 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ(373.15) = -31.83 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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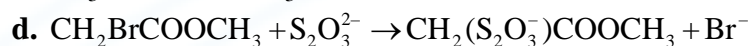
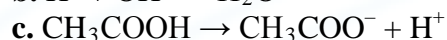
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**3.18.** Predict the signs of the entropy changes in the following reactions when they occur in aqueous solution.



**Solution:**

Given: **a.** Hydrolysis of urea:  $\text{H}_2\text{NCONH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3$



Required: signs of  $\Delta S$

**a)** For the hydrolysis of urea:

Simply by counting the number of molecules (or moles of each species) on either side of the reaction, it is evident that there is a positive entropy change. The system becomes ‘more disordered’ with an increase in the number of components on the product side.

$$\boxed{\Delta S = +}$$

**b)** For the formation of water:

Here, we are taking two molecules and putting them together. However, we must also consider the fact that initially, we are working with ions. These ions have electrostatic interactions with one another. Electrostriction is a property that dielectric materials possess. It is caused by the random alignment of electrical domains. Since the water molecule has less electrostatic interactions, the system becomes more ordered and there is a decrease in entropy.

$$\boxed{\Delta S = -}$$

**c)** For the decomposition of acetic acid:

We can use the same logic as we did in the previous example in order to answer part C. Since it is the reverse reaction, thus forming species with an increased amount of electrostriction; the system will become more ‘disordered’. This means that the change in entropy would be positive.

$$\Delta S = +$$

**d)** There is a decrease in electrostriction. Therefore, the the change in entropy is positive.

$$\Delta S = +$$

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**3.19.** Obtain a general expression, in terms of the molar heat capacity  $C_{P,m}$  and temperature  $T_1$  and  $T_2$ , for the entropy increase of  $n$  mol of a gas (not necessarily ideal) that is heated at constant pressure so that its temperature changes from  $T_1$  to  $T_2$ . To what does your expression reduce if the gas is ideal?

**Solution:**

Given:  $n = n$  mol,  $T_1$ ,  $T_2$

Required: general expression in terms of  $C_{P,m}$  and temperature

In Chapter 2, we saw Eq. 2.96 which states that:

$$\Delta H = C_{P,m} \Delta T$$

However, we know that under constant pressure, we can make the following substitution;

$$\Delta H = C_{P,m} \Delta T$$

$$q = \Delta H$$

$$q = C_{P,m} \Delta T \text{ or } dq = C_P dT$$

The corresponding entropy change is given by Eq. 3.68;

$$\Delta S = \int \frac{q_{\text{rev}}}{T} dT$$

$$\Delta S = \int \frac{C_P}{T} dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$\boxed{\Delta S = n \int_{T_1}^{T_2} \frac{C_{P,m}}{T} dT}$$

If we are assuming that the gas is ideal, then we can say that the heat capacity is independent of temperature (ie. it is constant) and the above expression reduces to;

$$\Delta S = n \int_{T_1}^{T_2} \frac{C_{P,m}}{T} dT$$

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

$$\boxed{\Delta S = nC_{P,m} \ln \frac{T_2}{T_1}}$$

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**3.20.** Initially 5 mol of an ideal gas, with  $C_{V,m} = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , are at a volume of  $5 \text{ dm}^3$  and a temperature of 300 K. If the gas is heated to 373 K and the volume changed to  $10 \text{ dm}^3$ , what is the entropy change?

**Solution:**

Given: Ideal Gas:  $n = 5 \text{ mol}$ ,  $C_{V,m} = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $V_1 = 5 \text{ dm}^3$ ,  $V_2 = 10 \text{ dm}^3$ ,  $T_1 = 300 \text{ K}$ ,  $T_2 = 373 \text{ K}$

Required:  $\Delta S$

We have already seen Eq. 3.55 which states:

$$dS = \frac{dq_{\text{rev}}}{T} = nC_{V,m} \frac{dT}{T} + nR \frac{dV}{V}$$

Upon integration and the assumption that  $C_{V,m}$  is independent of temperature we obtain Eq. 3.57,

$$\Delta S = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = (5.0 \text{ mol}) \left( 12.5 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{373 \text{ K}}{300 \text{ K}} + (5.0 \text{ mol}) \left( 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{10 \text{ dm}^3}{5 \text{ dm}^3}$$

$$\Delta S = (13.612 \ 247 + 28.815 \ 861) \text{ J K}^{-1}$$

$$\boxed{\Delta S = 42.4 \text{ J K}^{-1}}$$

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**\*3.21.** At 100 °C 200 g of mercury are added to 80 g of water at 20 °C in a vessel that has a water equivalent of 20 g. The specific heat capacities of water and mercury may be taken as constant at 4.18 and 0.140 J K<sup>-1</sup> g<sup>-1</sup>, respectively. Calculate the entropy change of (a) the mercury; (b) the water and vessel; (c) the mercury, water, and vessel together.

**Solution:**

Given:  $T = 100\text{ }^{\circ}\text{C}$ ,  $m_{\text{Hg}} = 200\text{ g}$ ,  $m_{\text{water/vessel}} = 100\text{ g}$ ,  $C_{\text{water}} = 4.18\text{ J K}^{-1}\text{ g}^{-1}$ ,  $C_{\text{Hg}} = 0.140\text{ J K}^{-1}\text{ g}^{-1}$

Required:  $\Delta S$  for a, b, c

We are told that the heat capacities for water and mercury are constant. This is like saying that they are independent of temperature and we will be able to use a form of Eq. 3.57 as we have done in the previous problem. First, let us determine the final temperature of the system;  $T''$ .

$$mC_p\Delta T$$

$$m_{\text{water}}C_p(T'' - T) = m_{\text{Hg}}C_p(T - T'')$$

$$(100\text{ g})(4.18\text{ J K}^{-1}\text{ g}^{-1})(T'' - 20)\text{ }^{\circ}\text{C} = (200\text{ g})(0.140\text{ J K}^{-1}\text{ g}^{-1})(100 - T'')\text{ }^{\circ}\text{C}$$

$$(418\text{ J K}^{-1})(T'' - 20)\text{ }^{\circ}\text{C} = (28\text{ J K}^{-1})(100 - T'')\text{ }^{\circ}\text{C}$$

$$(14.928\text{ }^{\circ}\text{C})(T'' - 20)\text{ }^{\circ}\text{C} = (100 - T'')\text{ }^{\circ}\text{C}$$

$$14.928\text{ }^{\circ}\text{C}T'' - 298.571\text{ }^{\circ}\text{C} = 100\text{ }^{\circ}\text{C} - T''$$

$$15.928\text{ }^{\circ}\text{C}T'' = 398.571\text{ }^{\circ}\text{C}$$

$$T'' = 25.02\text{ }^{\circ}\text{C}$$

**a)** Mercury: using a form of Eq. 3.55

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$\Delta S = mC_{P,m} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S = (200 \text{ g}) (0.140 \text{ J K}^{-1} \text{ g}^{-1}) \int_{373.15}^{298.17} \frac{dT}{T}$$

$$\Delta S = (28 \text{ J K}^{-1}) \ln \frac{298.17 \text{ K}}{373.15 \text{ K}}$$

$$\boxed{\Delta S = -6.28 \text{ J K}^{-1}}$$

b) Water and vessel: using a form of Eq. 3.55

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$\Delta S = mC_{P,m} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S = (100 \text{ g}) (4.18 \text{ J K}^{-1} \text{ g}^{-1}) \int_{293.15}^{298.17} \frac{dT}{T}$$

$$\Delta S = (418 \text{ J K}^{-1}) \ln \frac{298.17 \text{ K}}{293.15 \text{ K}}$$

$$\boxed{\Delta S = 7.10 \text{ J K}^{-1}}$$

c) Water, vessel and mercury:

$$\Delta S_{\text{net}} = \Delta S_{\text{Hg}} + \Delta S_{\text{water/vessel}}$$

$$\Delta S_{\text{net}} = (-6.28 + 7.10) \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}} = 0.82 \text{ J K}^{-1}}$$

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**\*3.22.** At 0 °C 20 g of ice are added to 50 g of water at 30°C in a vessel that has a water equivalent of 20 g. Calculate the entropy changes in the system and in the surroundings. The heat of fusion of ice at 0 °C is 6.02 kJ mol<sup>-1</sup>, and the specific heat capacities of water and ice may be taken as constant at 4.184 and 2.094 J K<sup>-1</sup> g<sup>-1</sup>, respectively, and independent of temperature.

**Solution:**

Given:  $T_{\text{ice}} = 0\text{ }^{\circ}\text{C}$ ,  $m_{\text{ice}} = 20\text{ g}$ ,  $m_{\text{water}} = 50\text{ g}$ ,  $T_{\text{water}} = 30\text{ }^{\circ}\text{C}$ ,  $m_{\text{vessel}} = 20\text{ g}$ ,

$$\Delta_{\text{fus}}H_{\text{ice}} = 6.02\text{ kJ mol}^{-1}, C_{\text{ice}} = 2.094\text{ J K}^{-1}\text{ g}^{-1}, C_{\text{water}} = 4.184\text{ J K}^{-1}\text{ g}^{-1}$$

Required:  $\Delta S$  for the system

In this particular problem, we will be dealing with different temperature ranges so it is important to first determine the amount of heat required to melt the ice or heat the water.

The heat required to melt 20 g of ice can be found by using the heat of fusion;

$$q = mC\Delta T$$

at constant  $T$ ,

$$q = n\Delta_{\text{fus}}H$$

$$n = \frac{m}{M}, M = 18.0152\text{ g mol}^{-1}$$

$$q = \frac{20\text{ g}}{18.0152\text{ g mol}^{-1}}(6020\text{ J mol}^{-1})$$

$$q = 6683.245\text{ J}$$

The heat required to warm up 20 g of water over a temperature range (use heat capacity);

$$q = mC\Delta T$$

$$q = mC_{\text{water}}\Delta T$$

$$q = (20\text{ g})(4.18\text{ J K}^{-1}\text{ g}^{-1})(T - 0)\text{ K}$$

$$q = 83.6T\text{ J}$$

The heat required to cool 70 g of water from 30 °C in the vessel to  $T$  °C (use heat capacity);

$$q = mC\Delta T$$

$$q = mC_{\text{water}}\Delta T$$

$$q = (70 \text{ g}) (4.18 \text{ J K}^{-1} \text{ g}^{-1}) (30 - T) \text{ K}$$

$$q = 292.6 \text{ J} (30 - T)$$

$$q = 8778 \text{ J} - 292.6 T$$

Now, we can balance out the reaction by writing:

$$n\Delta_{\text{fus}} H + mC_{\text{water}} (T - 0) = mC_{\text{water}} (30 - T)$$

$$(6683.245 \text{ J}) + (83.6 T \text{ J}) = 8778 \text{ J} - 292.6 T \text{ J}$$

Which can then be solved for  $T$ , we obtain;

$$n\Delta_{\text{fus}} H + mC_{\text{water}} (T - 0) = mC_{\text{water}} (30 - T)$$

$$(6683.245 \text{ J}) + (83.6 T \text{ J}) = 8778 \text{ J} - 292.6 T \text{ J}$$

$$83.6 T \text{ J} = 2094.755 \text{ J} - 292.6 T \text{ J}$$

$$376.2 T \text{ J} = 2094.755 \text{ J}$$

$$T = \frac{2094.755}{376.2}$$

$$T = 5.57 \text{ °C}$$

All of these processes are considered to be reversible and the heat capacities are independent of temperature (when working over a range).

Melting 20 g of ice at constant temperature:

$$\Delta S_{\text{syst}} = \frac{q}{T}$$

$$q = n\Delta_{\text{fus}}H \text{ and therefore,}$$

$$\Delta S_{\text{syst}} = \frac{n\Delta_{\text{fus}}H}{T} = \frac{m\Delta_{\text{fus}}H}{MT}$$

$$\Delta S_{\text{syst}} = \frac{(20 \text{ g})(6020 \text{ J mol}^{-1})}{(18.0152 \text{ g mol}^{-1})(273.15 \text{ K})}$$

$$\boxed{\Delta S_{\text{syst}} = 24.47 \text{ J K}^{-1}}$$

Due to the law of equilibrium,

$$dS^{\text{total}} = dS^{\text{syst}} + dS^{\text{surr}} = 0$$

$$dS^{\text{surr}} = -dS^{\text{syst}}$$

$$\boxed{\Delta S_{\text{surr}} = -24.47 \text{ J K}^{-1}}$$

Cooling 70 g of water to 0 °C:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$\Delta S_{\text{syst}} = mC_{P,m} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S_{\text{syst}} = (70 \text{ g}) \left( 4.184 \text{ J K}^{-1} \text{ g}^{-1} \right) \int_{303.15}^{273.15} \frac{dT}{T}$$

$$\Delta S_{\text{syst}} = (292.88 \text{ J K}^{-1}) \ln \frac{273.15 \text{ K}}{303.15 \text{ K}}$$

$$\boxed{\Delta S_{\text{syst}} = -30.52 \text{ J K}^{-1}}$$

$$\boxed{\Delta S_{\text{surr}} = 30.52 \text{ J K}^{-1}}$$

Heating the total amount of water (90 g) to the final temperature of the system:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$\Delta S_{\text{syst}} = m C_{P,m} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S_{\text{syst}} = (90 \text{ g}) (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \int_{273.15}^{278.72} \frac{dT}{T}$$

$$\Delta S_{\text{syst}} = (376.56 \text{ J K}^{-1}) \ln \frac{278.72 \text{ K}}{273.15 \text{ K}}$$

$$\boxed{\Delta S_{\text{syst}} = 7.60 \text{ J K}^{-1}}$$

$$\boxed{\Delta S_{\text{surr}} = -7.60 \text{ J K}^{-1}}$$

The net entropy change for this system will then be:

$$\Delta S_{\text{net}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_{\text{net}} = (24.47 - 30.52 + 7.60) \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}} (\text{syst}) = 1.55 \text{ J K}^{-1}}$$

$$\boxed{\Delta S_{\text{net}} (\text{surr}) = -1.55 \text{ J K}^{-1}}$$

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**\*3.23.** Calculate the increase in entropy of 1 mol of nitrogen if it is heated from 300 K to 1000 K at a constant pressure of 1 atm; use the  $C_P$  data in Table 2.1.

**Solution:**

Given:  $n_{\text{N}_2} = 1 \text{ mol}$ ,  $T_1 = 300 \text{ K}$ ,  $T_2 = 1000 \text{ K}$ ,  $P = 1 \text{ atm}$ , Table 2.1

Required:  $\Delta S_m$

The increase in entropy can be calculated by using Eq. 3.55, as well as information given in Chapter 2.

$$\Delta S_m = \int_{T_1}^{T_2} \frac{C_{P,m}}{T} dT$$

$$\text{(Eq. 2.48)} \quad C_{P,m} = d + eT + fT^{-2}$$

$$\Delta S_m = \int_{T_1}^{T_2} \frac{(d + eT + fT^{-2})}{T} dT$$

$$\Delta S_m = \int_{T_1}^{T_2} \frac{d}{T} dT + \int_{T_1}^{T_2} \frac{eT}{T} dT + \int_{T_1}^{T_2} \frac{fT^{-2}}{T} dT$$

$$\Delta S_m = d \ln \frac{1000}{300} + e(1000 - 300) + \frac{1}{2} f \left( \frac{1}{1000^2} - \frac{1}{300^2} \right)$$

$$\Delta S_m = \left[ (28.58) \ln \frac{1000}{300} + (0.00376 \times 700) + \frac{50000}{2} \left( \frac{1}{1000^2} - \frac{1}{300^2} \right) \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_m = 36.79 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**\*3.24.** The entropy change for the isothermal expansion of an ideal gas at 300 K from a particular state  $A$  to a state  $B$  is  $50 \text{ J K}^{-1}$ . When an expansion was performed, the work done by the system was 6 kJ. Was the process reversible or irreversible? If the latter, calculate the *degree of irreversibility* (i.e., the ratio of the work done to the reversible work).

**Solution:**

Given: Ideal Gas:  $T = 300 \text{ K}$  state A, state B is  $50 \text{ J K}^{-1}$ ,  $w(\text{by system}) = 6 \text{ kJ}$

Required: reversible or irreversible?

From Chapter 2, we have seen that for isothermal processes both the change in internal energy and enthalpy are equal to zero because they are dependent on temperature change. Let us first start by describing a reversible isothermal expansion.

$$\Delta U = q_{\text{rev}} + w_{\text{rev}}$$

$$\Delta U = 0$$

$$q_{\text{rev}} = -w_{\text{rev}}$$

$$\text{since } \Delta S = \frac{q_{\text{rev}}}{T} \text{ then,}$$

$$q_{\text{rev}} = T\Delta S$$

$$-w_{\text{rev}} = T\Delta S = (300 \text{ K})(50 \text{ J K}^{-1})$$

$$w_{\text{rev}} (\text{by system}) = 15\,000 \text{ J or } w_{\text{rev}} = -15\,000 \text{ J}$$

Given that the actual work done by the system is -6000 J which is less than the value we calculated above, we know that the process is an *irreversible one*.

The degree of irreversibility is therefore:

$$\frac{w_{\text{irr}}}{w_{\text{rev}}} = \frac{-6 \text{ kJ}}{-15 \text{ kJ}}$$

$$\boxed{\frac{w_{\text{irr}}}{w_{\text{rev}}} = 0.4}$$

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**3.25.** One mole of water is placed in surroundings at  $-3\text{ }^{\circ}\text{C}$ , but at first it does not freeze (it remains as supercooled water). Suddenly it freezes. Calculate the entropy change in the system during the freezing, making use of the following data:

$$C_{p,m}(\text{water}) = 75.3\text{ J K}^{-1}\text{ mol}^{-1}$$

$$C_{p,m}(\text{ice}) = 37.7\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta_f H(\text{ice} \rightarrow \text{water}) = 6.02\text{ kJ mol}^{-1}\text{ at } 0\text{ }^{\circ}\text{C}$$

The two  $C_p$  values can be assumed to be independent of temperature. Also, calculate the entropy change in the surroundings, and the net entropy change in the system and surroundings.

**Solution:**

Given:  $n_{\text{water}} = 1\text{ mol}$ ,  $T_{\text{surr}} = -3\text{ }^{\circ}\text{C}$ ,  $C_p$  values

Required:  $\Delta S$

In order to solve this problem, it is necessary to devise a process in which we can describe the freezing of water reversibly. This will take three steps;

(1) Heat the supercooled water reversibly from  $-3\text{ }^{\circ}\text{C}$  to  $0\text{ }^{\circ}\text{C}$ :

$$\Delta S_1 = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$\Delta S_1 = nC_{p,m} \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = (1.0\text{ mol}) \left( 75.3\text{ J K}^{-1}\text{ mol}^{-1} \right) \ln \frac{273.15\text{ K}}{270.15\text{ K}}$$

$$\boxed{\Delta S_1 = 0.831\text{ 593 J K}^{-1}}$$

(2) Freeze the water at  $0\text{ }^{\circ}\text{C}$  (use the enthalpy of formation):

$$\Delta S_2 = \frac{q}{T}$$

$$q = \Delta_{\text{fus}} H = -\Delta_f H$$

$$\Delta S_2 = \frac{-\Delta_f H}{T}$$

$$\Delta S_2 = \frac{-6020 \text{ J mol}^{-1}}{273.15 \text{ K}} \times 1 \text{ mol}$$

$$\boxed{\Delta S_2 = -22.04 \text{ J K}^{-1}}$$

(3) Cool the ice reversibly from 0 °C to -3 °C:

$$\Delta S_3 = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$\Delta S_3 = n C_{p,m} \ln \frac{T_2}{T_1}$$

$$\Delta S_3 = (1.0 \text{ mol}) (37.7 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{270.15 \text{ K}}{273.15 \text{ K}}$$

$$\boxed{\Delta S_3 = -0.416 \text{ 349 J K}^{-1}}$$

The net entropy change is therefore:

$$\Delta S_{\text{net}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_{\text{net}} = (0.831 \text{ 593} - 22.04 - 0.416 \text{ 349}) \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}} (\text{syst}) = -21.62 \text{ J K}^{-1}}$$

In order to determine the entropy change in the surroundings, we must first calculate all of the heat that has been gained by the environment in each step.

(1) Heat the supercooled water reversibly from -3 °C to 0 °C:

$$q_1 = nC_{p,m}\Delta T$$

$$q_1 = (1.0 \text{ mol}) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) (-3 - 0)$$

$$\boxed{q_1 = -225.9 \text{ J}}$$

(2) Freeze the water at 0 °C (use the enthalpy of formation):

$$\Delta_f H(\text{ice} \rightarrow \text{water}) = 6.01 \text{ kJ mol}^{-1}$$

$$q_2 = n\Delta_f H$$

$$\boxed{q_2 = 6020 \text{ J}}$$

(3) Cool the ice reversibly from 0 °C to -3 °C:

$$q_3 = nC_{p,m}\Delta T$$

$$q_3 = (1.0 \text{ mol}) (37.7 \text{ J K}^{-1} \text{ mol}^{-1}) (0 - (-3))$$

$$\boxed{q_3 = 113.1 \text{ J}}$$

The net heat gained by the surroundings is thus:

$$\Delta q_{\text{net}} = \Delta q_1 + \Delta q_2 + \Delta q_3$$

$$\Delta q_{\text{net}} = (-225.9 + 6020 + 113.1) \text{ J}$$

$$\boxed{\Delta q_{\text{net}} (\text{surr}) = 5907.2 \text{ J}}$$

The heat was gained by the surroundings at -3 °C and the entropy change is therefore given by:

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T}$$

$$\Delta S_{\text{surr}} = \frac{5907.2 \text{ J}}{270.15 \text{ K}} \times \text{mol}^{-1}$$

$$\boxed{\Delta S_{\text{surr}} = 21.87 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The net entropy change in the system and the surroundings is therefore:

$$\Delta S_{\text{net}} = \Delta S_{\text{net}}(\text{syst}) + \Delta S_{\text{net}}(\text{surr})$$

$$\Delta S_{\text{net}} = -21.62 \text{ J K}^{-1} + 21.87 \text{ J K}^{-1}$$

$$\Delta S_{\text{net}} = 0.25 \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}} = 0.25 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.26.** 200 cm<sup>3</sup> of a 0.5 mol solution of sucrose is diluted to 1 dm<sup>3</sup> by the addition of 800 cm<sup>3</sup> of water. Assume ideal behavior and calculate the entropy change.

**Solution:**

Given: Ideal:  $V_{\text{sucrose}} = 200 \text{ cm}^3$ ,  $n_{\text{sucrose}} = 0.5 \text{ mol}$ ,  $V_f = 1 \text{ dm}^3$ ,  $V_{\text{water}} = 800 \text{ cm}^3$

Required:  $\Delta S$

In the Ideal Gas section of Chapter 3, we have been given Eq. 3.51 which applies at constant temperature. Let us assume that this is true.

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

This means that we must first determine the number of moles and knowing that the total volume is 1000 cm<sup>3</sup> we can determine the entropy change.

$$n = 0.5 \frac{\text{mol}}{\cancel{\text{L}}} \times 1 \frac{\cancel{\text{L}}}{\text{dm}^3} \times 200 \cancel{\text{cm}^3} \times \frac{1 \cancel{\text{dm}^3}}{10^3 \cancel{\text{cm}^3}}$$

$$n = 0.1 \text{ mol}$$

$$\frac{V_f}{V_i} = \frac{1000 \cancel{\text{cm}^3}}{200 \cancel{\text{cm}^3}} = 5$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$\Delta S = (0.1 \cancel{\text{mol}}) (8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}}) \ln 5$$

$$\Delta S = 1.338 \, 167 \, 152 \text{ J K}^{-1}$$

$$\boxed{\Delta S = 1.34 \text{ J K}^{-1}}$$

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**3.27.** One liter of a 0.1 *M* solution of a substance A is added to 3 liters of a 0.05 *M* solution of a substance B. Assume ideal behavior and calculate the entropy of mixing.

**Solution:**

Given: Ideal:  $V_A = 1$  litre,  $C_A = 0.1$  M,  $V_B = 3$  litres,  $C_B = 0.05$  M

Required:  $\Delta S_{\text{mix}}$

Since we are working with liters and solution in Molar concentrations, we know that there are 0.1 moles of substance A and 0.15 moles of substance B. For substance A, the volume increases by a factor of 4. Let us again use Eq. 3.51 in order to calculate the entropy change.

$$\Delta S_A = nR \ln \frac{V_f}{V_A}$$

$$\Delta S_A = (0.1 \cancel{\text{mol}}) (8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}}) \ln \frac{4 \cancel{\text{L}}}{1 \cancel{\text{L}}}$$

$$\Delta S_A = 1.153 \text{ J K}^{-1}$$

For substance B, the volume increases by a factor of 4/3. This will give the following entropy change:

$$\Delta S_B = nR \ln \frac{V_f}{V_B}$$

$$\Delta S_B = (0.15 \cancel{\text{mol}}) (8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}}) \ln \frac{4 \cancel{\text{L}}}{3 \cancel{\text{L}}}$$

$$\Delta S_B = 0.359 \text{ J K}^{-1}$$

The entropy of mixing will therefore be given by the total entropy change for both substances A and B.

$$\Delta S_{\text{mix}} = \Delta S_A + \Delta S_B$$

$$\Delta S_{\text{mix}} = (1.153 + 0.359) \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{mix}} = 1.151 \text{ J K}^{-1}}$$

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**3.28.** Ten moles of water at 60 °C are mixed with an equal amount of water at 20 °C. Neglect any heat exchange with the surroundings and calculate the entropy change. The heat capacity of water may be taken to be  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$  and independent of temperature.

**Solution:**

Given:  $n_{\text{water}} = 10 \text{ mol}$ ,  $T = 60 \text{ °C}$ ,  $n_{\text{water2}} = 10 \text{ mol}$ ,  $T = 20 \text{ °C}$ ,  $C_p = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$

Required:  $\Delta S$

First it is important to determine the final temperature of the system. Since we are told that there is no heat exchange with the surroundings, we can simply take the average of the two temperatures which yields:

$$T_f = T_{\text{avg}} = \frac{(20 + 60) \text{ °C}}{2} = 40 \text{ °C}$$

The water at 60 °C can be cooled in a reversible manner to 40 °C while the water at 20 °C can be heated reversibly to the same final temperature. Since these processes are reversible, and the heat capacity is taken to be independent of temperature, we can use a form of Eq. 3.57 to determine the entropy change in either case.

$$\Delta S = nC_p \ln \frac{T_f}{T_i}$$

$$\Delta S_{60 \text{ °C}} = (10 \text{ mol}) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{313.15}{333.15}$$

$$\Delta S_{60 \text{ °C}} = -46.618 \text{ J K}^{-1}$$

$$\Delta S_{20 \text{ °C}} = (10 \text{ mol}) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{313.15}{293.15}$$

$$\Delta S_{20 \text{ °C}} = 49.696 \text{ J K}^{-1}$$

As we have previously seen, the net entropy change for the system is simply the addition of both entropy changes calculated above.



$$\Delta S = \Delta S_{\text{net}} = \Delta S_{60^\circ\text{C}} + \Delta S_{40^\circ\text{C}}$$

$$\Delta S = (-46.618\,629 + 49.696\,408) \text{ J K}^{-1}$$

$$\boxed{\Delta S = 3.08 \text{ J K}^{-1}}$$

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**3.29.** A vessel is divided by a partition into two compartments. One side contains 5 moles  $O_2$  at 1 atm pressure; the other, 5 moles  $N_2$  at 1 atm pressure. Calculate the entropy change when the partition is removed.

**Solution:**

Given: Side 1:  $n = 5$  mole  $O_2$ ,  $P = 1$  atm

Side 2:  $n = 5$  mole  $N_2$ ,  $P = 1$  atm

Required:  $\Delta S_{MIX} = -nR \sum_i x_i \ln x_i$

Treat the gases as Ideal Gases and since they are in contact they have the same temperature.

$$V_{O_2} = \frac{nRT}{P} = \frac{5RT}{1} = 5RT = V_{N_2} \equiv V$$

So both volumes are equal. Mole fractions,

$$x_{O_2} = \frac{5}{10} = \frac{1}{2} = x_{N_2}$$

$$\Delta S_{MIX} = -R \sum_i x_i \ln x_i = -R \frac{1}{2} \ln \frac{1}{2} - R \frac{1}{2} \ln \frac{1}{2} = R \ln 2$$

$$\Delta S_{MIX} = 5.76 \text{ e.u. per mole}$$

$$\Delta S_{MIX} = 10 \times 5.76 = 57.6 \text{ JK}^{-1}$$

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**3.30.** One mole of liquid water at 0 °C is placed in a freezer having a temperature of –12 °C. The water freezes and the ice cools to –12 °C. Making use of the data given in Problem 3.25, calculate the change in entropy in the system and in surroundings (the freezer), and the net entropy change.

**Solution:**

Given: data from 3.25,  $n_{\text{water}} = 1 \text{ mol}$ ,  $T = 0.00 \text{ °C}$ ,  $T_{\text{freezer}} = -12 \text{ °C}$

Required:  $\Delta S_{\text{net}}$

Just as was done in problem 3.25, we will consider this system as two reversible processes.

(1) The liquid water will freeze to become ice at 0 °C

$$\Delta S_1 = -\frac{\Delta_f H}{T}$$

$$\Delta S_1 = -\frac{6020 \text{ J mol}^{-1}}{273.15 \text{ K}}$$

$$\Delta S_1 = -22.039 \text{ J K}^{-1} \text{ mol}^{-1}$$

(2) The ice is cooled reversibly to -12 °C

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$\Delta S_2 = nC_{p,m} \ln \frac{T_2}{T_1}$$

$$\Delta S_2 = (1.0 \text{ mol}) \left( 37.7 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{261.15 \text{ K}}{273.15 \text{ K}}$$

$$\Delta S_2 = -1.693 \text{ J K}^{-1}$$

(3) Combine these values in order to determine the entropy change for the system

$$\Delta S(\text{system}) = \Delta S_1 + \Delta S_2$$

$$\Delta S(\text{system}) = (-22.039\,173 - 1.693\,715) \text{ J K}^{-1}$$

$$\boxed{\Delta S(\text{system}) = -23.73 \text{ J K}^{-1}}$$

It is important to calculate the amount of heat gained by the freezer.

$$q_1 = n\Delta_f H_{\text{ice}} = 6020 \text{ J}$$

$$q_2 = nC_{p,m}\Delta T = (1.0 \text{ mol})(37.7 \text{ J K}^{-1} \text{ mol}^{-1})(0 + 12) \text{ K}$$

$$q_2 = 452.4 \text{ J}$$

$$q_{\text{freezer}} = q_1 + q_2$$

$$q_{\text{freezer}} = (6020 + 452.4) \text{ J}$$

$$q_{\text{freezer}} = 6472.4 \text{ J}$$

Since this heat was gained at  $-12^\circ\text{C}$ , we can define the entropy change as:

$$\Delta S_{\text{freezer}}(\text{surr}) = \frac{q_{\text{freezer}}}{T}$$

$$\Delta S_{\text{freezer}}(\text{surr}) = \frac{6472.4 \text{ J}}{261.15 \text{ K}}$$

$$\boxed{\Delta S_{\text{freezer}}(\text{surr}) = 24.78 \text{ J K}^{-1}}$$

The net entropy change occurring in the system and surrounding is therefore,

$$\Delta S_{\text{net}}(\text{total}) = \Delta S_{\text{net}}(\text{system}) + \Delta S_{\text{net}}(\text{surr})$$

$$\Delta S_{\text{net}}(\text{total}) = (-23.73 + 24.78) \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}}(\text{total}) = 1.05 \text{ J K}^{-1}}$$

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**3.31.** One mole of liquid water at 0 °C is placed in a freezer which is maintained at -10 °C. Carry out the same calculations as for Problem 3.30.

**Solution:**

Given:  $n_{\text{water}} = 1 \text{ mol}$ ,  $T = 0.00 \text{ °C}$ ,  $T_{\text{freezer}} = -10 \text{ °C}$

Required:  $\Delta S_{\text{net}}$

Just as was done in problem 3.25, we will consider this system as two reversible processes.

(1) The liquid water will freeze to become ice at 0 °C

$$\Delta S_1 = -\frac{\Delta_f H}{T}$$

$$\Delta S_1 = -\frac{6020 \text{ J mol}^{-1}}{273.15 \text{ K}}$$

$$\Delta S_1 = -22.039 \text{ J K}^{-1} \text{ mol}^{-1}$$

(2) The ice is cooled reversibly to -10 °C

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$\Delta S_2 = nC_{p,m} \ln \frac{T_2}{T_1}$$

$$\Delta S_2 = (1.0 \text{ mol}) (37.7 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{263.15 \text{ K}}{273.15 \text{ K}}$$

$$\Delta S_2 = -1.406 \text{ J K}^{-1}$$

(3) Combine these values in order to determine the entropy change for the system

$$\Delta S(\text{system}) = \Delta S_1 + \Delta S_2$$

$$\Delta S(\text{system}) = (-22.039\,173 - 1.406\,092) \text{ J K}^{-1}$$

$$\boxed{\Delta S(\text{system}) = -23.45 \text{ J K}^{-1}}$$

It is important to calculate the amount of heat gained by the freezer.

$$q_1 = n\Delta_f H_{\text{ice}} = 6020 \text{ J}$$

$$q_2 = nC_{p,m}\Delta T = (1.0 \text{ mol})(37.7 \text{ J K}^{-1} \text{ mol}^{-1})(0 + 10) \text{ K}$$

$$q_2 = 377 \text{ J}$$

$$q_{\text{freezer}} = q_1 + q_2$$

$$q_{\text{freezer}} = (6020 + 377) \text{ J}$$

$$q_{\text{freezer}} = 6397 \text{ J}$$

Since this heat was gained at  $-10^\circ\text{C}$ , we can define the entropy change as:

$$\Delta S_{\text{freezer}}(\text{surr}) = \frac{q_{\text{freezer}}}{T}$$

$$\Delta S_{\text{freezer}}(\text{surr}) = \frac{6397 \text{ J}}{263.15 \text{ K}}$$

$$\boxed{\Delta S_{\text{freezer}}(\text{surr}) = 24.31 \text{ J K}^{-1}}$$

The net entropy change occurring in the system and surrounding is therefore,

$$\Delta S_{\text{net}}(\text{total}) = \Delta S_{\text{net}}(\text{system}) + \Delta S_{\text{net}}(\text{surr})$$

$$\Delta S_{\text{net}}(\text{total}) = (-23.45 + 24.31) \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}}(\text{total}) = 0.86 \text{ J K}^{-1}}$$

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**3.32.** Two moles of water at 60 °C are added to 4 mol of water at 20 °C. Calculate the entropy change, assuming that there is no loss of heat to the surroundings. The heat capacity of water is  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Solution:**

Given:  $n_{\text{water}} = 2 \text{ mol}$ ,  $T_{\text{water}} = 60 \text{ °C}$ ,  $n_{\text{water2}} = 4 \text{ mol}$ ,  $T_{\text{water2}} = 20 \text{ °C}$ ,  $C_p = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$

Required:  $\Delta S$

This problem may be solved by using a similar method to problem 3.21. It is important to determine the final temperature of the system after the mixing occurs. Since we are not neglecting the heat exchange between the system and the surroundings, we cannot use the same method as in problem 3.28.

$$nC_p \Delta T$$

$$n_{\text{water1}} C_p (T_1 - T) = n_{\text{water2}} C_p (T_2 - T)$$

$$(2.0 \text{ mol})(75.3 \text{ J K}^{-1} \text{ mol}^{-1})(60 - T)^\circ \text{C} = (4.0 \text{ mol})(75.3 \text{ J K}^{-1} \text{ mol}^{-1})(T - 20)^\circ \text{C}$$

$$(150.6 \text{ J K}^{-1})(60 - T) = (301.2 \text{ J K}^{-1})(T - 20)$$

$$(60 - T) = 2(T - 20)$$

$$60 - T = 2T - 40$$

$$100 = 3T$$

$$T = 33.333 \text{ 333 33 }^\circ \text{C}$$

$$T = 306.483 \text{ 333 3 K}$$

$$T = 306.48 \text{ K}$$

Since the heat capacity is taken to be independent of temperature, we can use a form of Eq. 3.57 to determine the entropy change.

$$\Delta S = nC_p \ln \frac{T_f}{T_i}$$

$$\Delta S_{60^\circ\text{C}} = (2.0 \text{ mol}) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{306.48 \text{ K}}{333.15 \text{ K}}$$

$$\Delta S_{60^\circ\text{C}} = -12.566 \text{ 115 J K}^{-1}$$

$$\Delta S_{20^\circ\text{C}} = (4.0 \text{ mol}) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{306.48 \text{ K}}{293.15 \text{ K}}$$

$$\Delta S_{20^\circ\text{C}} = 13.393 \text{ 784 79 J K}^{-1}$$

As we have previously seen, the net entropy change for the system is simply the addition of both entropy changes calculated above.

$$\Delta S = \Delta S_{\text{net}} = \Delta S_{60^\circ\text{C}} + \Delta S_{20^\circ\text{C}}$$

$$\Delta S = (-12.566 \text{ 115} + 13.393 \text{ 784 79}) \text{ J K}^{-1}$$

$$\Delta S = 0.827 \text{ 669 794 J K}^{-1}$$

$$\boxed{\Delta S = 0.828 \text{ J K}^{-1}}$$

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**3.33.** One mole of an ideal gas is initially at 10 bar and 298 K. It is allowed to expand against a constant external pressure of 2 bar to a final pressure of 2 bar. During this process, the temperature of the gas falls to 253.2 K. Find  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S_{\text{therm}}$ , and  $\Delta S_{\text{univ}}$  for the process. Assume that the thermal surroundings remain at 298 K throughout. Devise at least three different paths to accomplish this change and show that no matter which path is used, the desired values are the same.

**Solution:**

Given: Ideal Gas:  $n = 1$  mol,  $P_i = 10$  bar,  $T_i = 298$  K,  $P_{\text{ext}} = 2$  bar,  $P_f = 2$  bar,  $T_f = 253.2$  K

$$T_{\text{surr}} = 298 \text{ K}$$

Required:  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S_{\text{therm}}$ , and  $\Delta S_{\text{univ}}$ , devise three different paths

It is important to consider the fact that there are many reversible paths that can be taken in order to move from the initial to final state. We will consider four of them.

1. It is possible to perform an *isothermal expansion* to the final volume. After this, we should cool the gas at *constant volume* until we reach the final temperature.

$\Delta U = 0$  we know that this is true because there is neither a change in internal energy or enthalpy when an ideal gas is subject to isothermal conditions.

$\Delta U = C_{V,m}(T_f - T_i)$  is also true for the second part of this process (under constant volume).

By putting these two expressions together we can generate the change in internal energy for this pathway.

$$\Delta U = 0 + C_{V,m}(T_f - T_i)$$

$$C_{V,m} = \frac{3}{2}R$$

$$\Delta U = \frac{3}{2}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(253.2 - 298) \text{ K}$$

$$\boxed{\Delta U = -558.7 \text{ J mol}^{-1}}$$

$$\Delta H = 0 + C_{P,m}(T_f - T_i)$$

$$C_{P,m} = \frac{5}{2}R$$

$$\Delta H = \frac{5}{2}(8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1})(253.2 - 298) \cancel{\text{K}}$$

$$\boxed{\Delta H = -931.2 \text{ J mol}^{-1}}$$

Under constant temperature, we have seen (from Eq. 3.94) that the entropy is given as:

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Similarly, at constant volume, the following expression holds true;

$$\Delta S = C_{V,m} \ln \frac{T_f}{T_i}$$

$$\Delta S = R \ln \frac{V_f}{V_i} + C_{V,m} \ln \frac{T_f}{T_i}$$

$$PV = nRT$$

$$V_i = \frac{nRT_i}{P_i} = \frac{(1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{10 \text{ bar}} = 247.7721 \text{ J bar}^{-1}$$

$$1 \text{ bar} = 10^5 \text{ Pa}, 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}, 1 \text{ atm dm}^3 = 101.325 \text{ J}$$

$$V_i = 247.7721 \cancel{\text{ J bar}^{-1}} \times \frac{1 \cancel{\text{ bar}}}{10^5 \cancel{\text{ Pa}}} \times \frac{1.01325 \times 10^5 \cancel{\text{ Pa}}}{1 \cancel{\text{ atm}}} \times \frac{1 \cancel{\text{ atm dm}^3}}{101.325 \cancel{\text{ J}}}$$

$$V_i = 2.477\,721 \text{ dm}^3$$

$$V_f = \frac{nRT_f}{P_f} = \frac{(1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(253.2 \text{ K})}{2 \text{ bar}} = 1052.6157 \text{ J bar}^{-1}$$

$$V_f = 1052.6157 \cancel{\text{ J bar}^{-1}} \times \frac{1 \cancel{\text{ bar}}}{10^5 \cancel{\text{ Pa}}} \times \frac{1.01325 \times 10^5 \cancel{\text{ Pa}}}{1 \cancel{\text{ atm}}} \times \frac{1 \cancel{\text{ atm dm}^3}}{101.325 \cancel{\text{ J}}}$$

$$V_f = 10.526\,157 \text{ dm}^3$$

$$\Delta S = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{10.526\,157}{2.477\,721} + \frac{3}{2} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{253.2}{298}$$

$$\Delta S = 12.027\,125 \text{ J K}^{-1} \text{ mol}^{-1} - 2.031\,820 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S = 9.995 \text{ J K}^{-1} \text{ mol}^{-1}}$$

2. The second method to arrive at the final state entails an *isothermal expansion to the final pressure*. We can then employ *constant pressure cooling* in order to attain the final temperature.

$\Delta U = 0$  we know that this is true because there is neither a change in internal energy or enthalpy when an ideal gas is subject to isothermal conditions.

$\Delta U = C_{V,m}(T_f - T_i)$  is also true for the second part of this process (just as we have seen for constant volume!)

By putting these two expressions together we can generate the change in internal energy for this pathway.

$$\Delta U = 0 + C_{V,m}(T_f - T_i)$$

$$C_{V,m} = \frac{3}{2}R$$

$$\Delta U = \frac{3}{2}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(253.2 - 298) \text{ K}$$

$$\boxed{\Delta U = -558.7 \text{ J mol}^{-1}}$$

$$\Delta H = 0 + C_{P,m}(T_f - T_i)$$

$$C_{P,m} = \frac{5}{2}R$$

$$\Delta H = \frac{5}{2}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(253.2 - 298) \text{ K}$$

$$\boxed{\Delta H = -931.2 \text{ J mol}^{-1}}$$

Since we know that pressure and volume have an inverse relationship, we can simply write:

$\Delta S = R \ln \frac{P_i}{P_f}$  when we are carrying out the expansion under constant pressure (rather than constant volume). The second part of the pathway will remain the same aside from the fact that we will be using  $C_{P,m}$ .

$$\Delta S = R \ln \frac{P_i}{P_f} + C_{P,m} \ln \frac{T_f}{T_i}$$

$$C_{P,m} = \frac{5}{2}R$$

$$\Delta S = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{10}{2} + \frac{5}{2}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{253.2}{298}$$

$$\boxed{\Delta S = 9.995 \text{ J K}^{-1} \text{ mol}^{-1}}$$

3. The third path will involve an isothermal expansion from  $(P_0, V_0)$  followed by an adiabatic expansion to the final state.

It is important to note that we need to find the intersection of the isotherm that passes through the initial state and the adiabat that passes through the final state. This intersection is  $(P_0, V_0)$  at  $T_i$ . Using the relationships for adiabatic processes (Eq. 2.90);

$$\frac{T_f}{T_i} = \left( \frac{V_0}{V_f} \right)^{\gamma-1}$$

$$\gamma = \frac{C_{P,m}}{C_{V,m}} \text{ and } C_{P,m} = \frac{5}{2}R, \quad C_{V,m} = \frac{3}{2}R$$

$$\gamma = \frac{\frac{5}{2} \cancel{K}}{\frac{3}{2} \cancel{K}} \rightarrow \frac{5}{\cancel{2}} \times \frac{\cancel{2}}{3} \rightarrow \frac{5}{3}$$

$$\frac{T_f}{T_i} = \left( \frac{V_0}{V_f} \right)^{\frac{2}{3}} \rightarrow \left( \frac{T_f}{T_i} \right)^{\frac{3}{2}} = \left( \frac{V_0}{V_f} \right)$$

$$V_0 = V_f \left( \frac{T_f}{T_i} \right)^{\frac{3}{2}} = 10.526 \text{ dm}^3 \left( \frac{253.2 \cancel{K}}{298 \cancel{K}} \right)^{\frac{3}{2}}$$

$$V_0 = 8.243 \text{ 934 dm}^3$$

$$\Delta U = 0 + C_{V,m}(T_f - T_i)$$

$$C_{V,m} = \frac{3}{2}R$$

$$\Delta U = \frac{3}{2} \left( 8.3145 \text{ J } \cancel{K} \text{ mol}^{-1} \right) (253.2 - 298) \cancel{K}$$

$$\boxed{\Delta U = -558.7 \text{ J mol}^{-1}}$$

$$\Delta H = 0 + C_{P,m}(T_f - T_i)$$

$$C_{P,m} = \frac{5}{2}R$$

$$\Delta H = \frac{5}{2}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(253.2 - 298) \text{ K}$$

$$\boxed{\Delta H = -931.2 \text{ J mol}^{-1}}$$

When determining the change in entropy, we can use the first part of the equation given in the first method, however, during the adiabatic expansion, there will be no change in entropy.

$$\Delta S = R \ln \frac{V_o}{V_i} + 0$$

$$\Delta S = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{8.243 \text{ 934 dm}^3}{2.477 \text{ 721 dm}^3}$$

$$\boxed{\Delta S = 9.995 \text{ J K}^{-1} \text{ mol}^{-1}}$$

4. Constant pressure heating to the final volume followed by constant volume cooling to the final pressure.

The gas will have to be heated to  $T_o = 1266.0 \text{ K}$  in order for it to reach the volume of  $10.526 \text{ dm}^3$  at  $10.0 \text{ bar}$  pressure. Therefore;

$$\Delta U = C_{V,m}(T_o - T_i) + C_{V,m}(T_f - T_o) = \frac{3}{2}R(1266.0 - 298.1 + 253.2 - 1266.0)$$

$$\boxed{\Delta U = -558.7 \text{ J mol}^{-1}}$$

$$\Delta H = C_{P,m}(T_o - T_i) + C_{P,m}(T_f - T_o) = \frac{5}{2}R(1266.0 - 298.1 + 253.2 - 1266.0)$$

$$\boxed{\Delta H = -931.2 \text{ J mol}^{-1}}$$

$$\Delta S = C_{P,m} \ln \left( \frac{T_o}{T_i} \right) + C_{V,m} \ln \left( \frac{T_f}{T_o} \right) = \frac{5}{2}R \ln \left( \frac{1266.0}{298.0} \right) + \frac{3}{2}R \ln \left( \frac{253.2}{1266.0} \right)$$

$$\boxed{\Delta S = 9.995 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Yet another path we can try is constant volume cooling to the final pressure followed by constant pressure heating to the final temperature.

In each of these cases, we have verified that  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  are the same, thus proving that they are independent of the path taken, as any state property should be. We now have to find the entropy change of the surroundings.

The actual process is the expansion of the gas against a constant external pressure of 2 bar. For this process, according to the first law,

$$\Delta U = q_{act} - P_{ext} (V_f - V_i); \text{ Therefore,}$$

$$q_{act} = \Delta U + P_{ext} (V_f - V_i)$$

$$q_{act} = (-558.7 \text{ J mol}^{-1}) + (2.0 \text{ bar}) \times (10.526 - 2.478) \frac{\text{dm}^3}{\text{mol}} \times \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}}$$

$$q_{act} = 1050.9 \text{ J mol}^{-1}$$

$$\Delta S_{\text{surr}} = \frac{-q_{act}}{T_{\text{surr}}} = \frac{-1050.9 \text{ J mol}^{-1}}{298 \text{ K}}$$

$$\Delta S_{\text{surr}} = -3.526 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_{\text{surr}} = -3.527 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}} = (9.995 - 3.527) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_{\text{univ}} = 6.468 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.34.** Five moles of water at 50 °C are placed in a refrigerator maintained at 3 °C. Calculate  $\Delta S$  for the system and for the environment, and the net entropy change, taking  $C_P$  for water at 75.3 J K<sup>-1</sup> mol<sup>-1</sup> and independent of temperature.

**Solution:**

Given:  $n_{\text{water}} = 5 \text{ mol}$ ,  $T_{\text{water}} = 50 \text{ °C}$ ,  $T_{\text{fridge}} = 3 \text{ °C}$ ,  $C_P = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$

Required:  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{fridge (surr)}}$ ,  $\Delta S_{\text{net}}$

(1) Since the heat capacity is independent of temperature, the entropy change for the system can be defined by,

$$\Delta S_{\text{sys}} = nC_P \ln \frac{T_{\text{fridge}}}{T_{\text{water}}}$$

$$\Delta S_{\text{sys}} = (5.0 \text{ mol}) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{276.15}{323.15}$$

$$\Delta S_{\text{sys}} = -59.175 \text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{sys}} = -59.18 \text{ J K}^{-1}}$$

(2) The heat accepted by the fridge can now be found.

$$q_{\text{fridge}} = nC_{P,m} \Delta T$$

$$q_{\text{fridge}} = (5.0 \text{ mol}) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) (323.15 - 276.15) \text{ K}$$

$$q_{\text{fridge}} = 17695.5 \text{ J}$$

(3) Since this heat was gained at 3 °C, we can define the entropy change as:



$$\Delta S_{\text{fridge}}(\text{surr}) = \frac{q_{\text{fridge}}}{T}$$

$$\Delta S_{\text{fridge}}(\text{surr}) = \frac{19695.5 \text{ J}}{276.15 \text{ K}}$$

$$\Delta S_{\text{fridge}}(\text{surr}) = 64.079 \text{ 304 73 J K}^{-1}$$

$$\boxed{\Delta S_{\text{fridge}}(\text{surr}) = 64.08 \text{ J K}^{-1}}$$

The net entropy change between the system and surroundings is therefore,

$$\Delta S_{\text{net}}(\text{total}) = \Delta S_{\text{sys}} + \Delta S_{\text{fridge}}(\text{surr})$$

$$\Delta S_{\text{net}}(\text{total}) = (-59.175 \text{ 414 38} + 64.079 \text{ 304 73}) \text{ J K}^{-1}$$

$$\Delta S_{\text{net}}(\text{total}) = 4.903 \text{ 890 346 J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}}(\text{total}) = 4.90 \text{ J K}^{-1}}$$

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**3.35.** Problem 2.32 of Chapter 2 was concerned with dropping (a) one ice cube, (b) 10 ice cubes, each weighing 100 g, into 1 kg of water at 20 °C. Calculate the entropy change in each case. ( $\Delta H_{\text{fus}}$  of ice at 0 °C is 6.026 kJ mol<sup>-1</sup>;  $C_{P,m}$  for water is 75.3 J K<sup>-1</sup> mol<sup>-1</sup>.)

**Solution:**

Given: Problem 2.32

Required:  $\Delta S$  in each case

**a)** Recall that in the first case (only one ice cube), all of the ice melts and the final temperature was 12 °C (see solution to problem 2.32). The entropy change associated with this process can be broken down into three reversible processes.

(1) The ice melts reversibly at 0 °C

$$\Delta S_1 = \frac{n\Delta_f H_{\text{ice}}}{T}$$

$$n = \frac{m}{M} = \frac{100 \cancel{\text{g}}}{18.0152 \cancel{\text{g}} \text{ mol}^{-1}} = 5.550\,868 \text{ mol}$$

$$\Delta S_1 = \frac{(5.550\,868 \cancel{\text{mol}})(6025 \text{ J } \cancel{\text{mol}^{-1}})}{273.15 \text{ K}}$$

$$\Delta S_1 = 122.438\,150 \text{ J K}^{-1}$$

(2) The water is heated reversibly from 0 °C to 12 °C

$$\Delta S_2 = nC_p \ln \frac{T_f}{T_i}$$

$$\Delta S_2 = (5.550\,868 \cancel{\text{mol}})(75.3 \text{ J K}^{-1} \cancel{\text{mol}^{-1}}) \ln \frac{285.15}{273.15}$$

$$\Delta S_2 = 17.970\,757 \text{ J K}^{-1}$$

(3) 1 kg of water is cooled reversibly from 20 °C to 12 °C

$$\Delta S_3 = nC_p \ln \frac{T_f}{T_i}$$

$$\Delta S_3 = (55.508\,682\,\text{mol}) (75.3\,\text{J K}^{-1}\,\text{mol}^{-1}) \ln \frac{285.15}{293.15}$$

$$\Delta S_3 = -115.651\,264\,\text{J K}^{-1}$$

The net entropy change is therefore given by the sum of the entropies calculated above.

$$\Delta S_{\text{net}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_{\text{net}} = (122.438\,150 + 17.970\,757 - 115.651\,264)\,\text{J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}} = 24.76\,\text{J K}^{-1}}$$

**b)** In the second situation, only 250 g of the ice melts and the final temperature of the water ends up being 0 °C (see solution to problem 2.32). Using the same method as above, we will break the system down into two reversible processes.

(1) 250 g of ice melts reversibly at 0 °C

$$\Delta S_1 = \frac{n\Delta_f H_{\text{ice}}}{T}$$

$$n = \frac{m}{M} = \frac{250\,\cancel{\text{g}}}{18.0152\,\cancel{\text{g}}\,\text{mol}^{-1}} = 13.877\,170\,\text{mol}$$

$$\Delta S_1 = \frac{(13.877\,170\,\text{mol})(6025\,\text{J mol}^{-1})}{273.15\,\text{K}}$$

$$\Delta S_1 = 306.095\,375\,\text{J K}^{-1}$$

(2) 1 kg of water is cooled reversibly from 20 °C to 0 °C

$$\Delta S_2 = nC_p \ln \frac{T_f}{T_i}$$

$$\Delta S_2 = (55.508\,682\text{ mol}) (75.3\text{ J K}^{-1}\text{ mol}^{-1}) \ln \frac{273.15}{293.15}$$

$$\Delta S_2 = -295.358\,845\text{ J K}^{-1}$$

The net entropy change is therefore given by the sum of the entropies calculated above.

$$\Delta S_{\text{net}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_{\text{net}} = (306.095\,375 - 295.358\,845\text{ J K}^{-1})\text{ J K}^{-1}$$

$$\boxed{\Delta S_{\text{net}} = 10.74\text{ J K}^{-1}}$$

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**3.36.** The absolute entropy of nitrogen at its vaporization point of 77.32 K and exactly 1 bar is  $151.94 \text{ J K}^{-1} \text{ mol}^{-1}$ . Using the expression for  $C_{P,m}$  for nitrogen given in Table 2.1, find the entropy of the gas at 800.0 K and 1 bar.

**Solution:**

Given:  $\Delta_{\text{abs}} S_{\text{N}_2} = 151.94 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T_{\text{vap}} = 77.32 \text{ K}$ ,  $P = 1 \text{ bar}$ , Table 2.1

Required:  $\Delta S$  of gas

In Eq. 2.48 we are given the following expression for  $C_{P,m}$ :

$$C_{P,m} = d + eT + fT^{-2}$$

For nitrogen at 800 K and 1 bar, we are given that;

$$d = 28.58 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$e = 3.76 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$f = -5.0 \times 10^4 \text{ J K mol}^{-1}$$

We can substitute the expression for  $C_{P,m}$  into the equation that produces the value for entropy at a single given temperature.

$$S^\circ(800 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = \Delta_{\text{abs}} S^\circ + \int_{T_i}^{T_f} \frac{C_{P,m}}{T} dT$$

$$S^\circ(800 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 151.94 + \int_{77.32 \text{ K}}^{800 \text{ K}} \frac{(28.58 + 3.76 \times 10^{-3} T - 5.0 \times 10^4 / T^2)}{T} dT$$

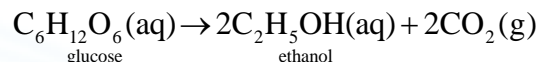
$$S^\circ(800 \text{ K}) = 151.94 + \left\{ \int_{77.32 \text{ K}}^{800 \text{ K}} \frac{(28.58)}{T} dT + \int_{77.32 \text{ K}}^{800 \text{ K}} \frac{(3.76 \times 10^{-3} T)}{T} dT - \int_{77.32 \text{ K}}^{800 \text{ K}} \frac{(5.0 \times 10^4 / T^2)}{T} dT \right\}$$

$$\boxed{S^\circ(800 \text{ K}) = 217.3 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.37.** Calculate  $\Delta G^\circ$  at 25 °C for the following fermentation reaction:



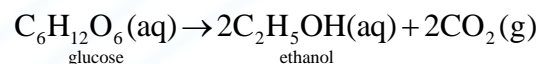
The standard Gibbs energies of formation of glucose, ethanol, and carbon dioxide are given in Appendix D. Also use the data in Appendix D to calculate  $\Delta S^\circ$  for the fermentation reaction.

**Solution:**

Given: Appendix D

Required:  $\Delta G^\circ$ ,  $\Delta S^\circ$

By using Appendix D and Eq. 3.91, we will be able to determine the standard change in Gibbs Energy. Given that;



$$\Delta_f G(\text{C}_6\text{H}_{12}\text{O}_6, \text{aq}) = -910.4 \text{ kJ mol}^{-1}$$

$$\Delta_f G(\text{C}_2\text{H}_5\text{OH}, \text{aq}) = -181.64 \text{ kJ mol}^{-1}$$

$$\Delta_f G(\text{CO}_2, \text{g}) = -394.36 \text{ kJ mol}^{-1}$$

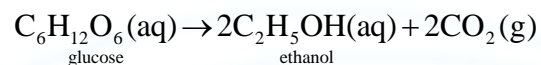
$$\Delta G^\circ = \sum \Delta_f G(\text{products}) - \sum \Delta_f G(\text{reactants})$$

$$\Delta G^\circ = 2\Delta_f G(\text{CO}_2, \text{g}) + 2\Delta_f G(\text{C}_2\text{H}_5\text{OH}, \text{aq}) - \Delta_f G(\text{C}_6\text{H}_{12}\text{O}_6, \text{aq})$$

$$\Delta G^\circ = (2 \times -394.36 \text{ kJ mol}^{-1}) + (2 \times -181.64 \text{ kJ mol}^{-1}) - (-910.4 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta G^\circ = -241.6 \text{ kJ mol}^{-1}}$$

We may also use Appendix D and a similar equation for the standard enthalpy change in order to determine the standard entropy change.



$$\Delta_f H(\text{C}_6\text{H}_{12}\text{O}_6, \text{aq}) = -1273.3 \text{ kJ mol}^{-1}$$

$$\Delta_f H(\text{C}_2\text{H}_5\text{OH}, \text{aq}) = -288.3 \text{ kJ mol}^{-1}$$

$$\Delta_f H(\text{CO}_2, \text{g}) = -393.51 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$$

$$\Delta H^\circ = 2\Delta_f H(\text{CO}_2, \text{g}) + 2\Delta_f H(\text{C}_2\text{H}_5\text{OH}, \text{aq}) - \Delta_f H(\text{C}_6\text{H}_{12}\text{O}_6, \text{aq})$$

$$\Delta H^\circ = (2 \times -393.51 \text{ kJ mol}^{-1}) + (2 \times -288.3 \text{ kJ mol}^{-1}) - (-1273.3 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta H^\circ = -90.32 \text{ kJ mol}^{-1}}$$

Rearranging the Gibbs Free Energy equation, we obtain,

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{[-90.32 - (-241.6)] \text{ kJ mol}^{-1}}{298.15 \text{ K}}$$

$$\boxed{\Delta S^\circ = 507.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.38.** The latent heat of vaporization of water at 100 °C is 40.6 kJ mol<sup>-1</sup> and when 1 mol of water is vaporized at 100 °C and 1 atm pressure, the volume increase is 30.19 dm<sup>3</sup>. Calculate the work done by the system, the change in internal energy  $\Delta U$ , the change in Gibbs energy  $\Delta G$  and the entropy change  $\Delta S$ .

**Solution:**

Given:  $\Delta_{\text{vap}}H = 40.6 \text{ kJ mol}^{-1}$ ,  $T = 100 \text{ }^{\circ}\text{C}$ ,  $n_{\text{water}} = 1 \text{ mol}$ ,  $P = 1 \text{ atm}$ ,  $\Delta V = 30.19 \text{ dm}^3$

Required:  $w$ ,  $\Delta U$ ,  $\Delta G$ ,  $\Delta S$

Since there is pressure-volume work done on the system, we can determine the work done according to;

$$w = P\Delta V$$

$$w = (1 \text{ atm})(30.19 \text{ dm}^3)$$

$$w = 30.19 \text{ atm dm}^3$$

1 atm dm<sup>3</sup> = 101.325 J therefore,

$$w = 30.19 \cancel{\text{ atm dm}^3} \times \frac{101.325 \text{ J}}{1 \cancel{\text{ atm dm}^3}}$$

$$w = 3059 \text{ J}$$

Since it is already for 1 mole of water then we can say that,

$$\boxed{w = 3059 \text{ J mol}^{-1}}$$

Recall from Chapter 2 the following equation,

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta U = \Delta H - \Delta(PV)$$

$$\Delta U = 40\,600 \text{ J mol}^{-1} - 3059 \text{ J mol}^{-1}$$

$$\boxed{\Delta U = 37\,541 \text{ J mol}^{-1}}$$



Let us now use the Gibbs Free Energy equation:

$$\Delta G = \Delta H - T \Delta S$$

$$\boxed{\Delta G = 0}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$\Delta S = \frac{40\,600 \text{ J mol}^{-1}}{373.15 \text{ K}} \rightarrow \boxed{\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.39.** On pages 115–116 we worked out the  $\Delta S$  values for the freezing of water at 0 °C and at –10 °C. What are the corresponding  $\Delta G$  values?

**Solution:**

Given: pages 115-116

Required:  $\Delta G$  values

Using Example 3.6 on page 115, we can see that the enthalpy and entropy values have already been worked out. We can therefore determine the change in Gibbs Free Energy by using our well known equation which will be given below. From the text we have;

a) The entropy change in the reversible freezing water at 0 °C :

$$\Delta S_2 = -\frac{q_{\text{fus}}}{T} = -\frac{6020 \text{ J mol}^{-1}}{273.15 \text{ K}}$$

$$\Delta S_2 = -22.039 \text{ 172 62 J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_{\text{fus}} H = q_{\text{fus}}$$

$$\Delta_{\text{fus}} H = 6.02 \text{ kJ mol}^{-1}$$

$$\Delta H (\text{freezing}) = -6.02 \text{ kJ mol}^{-1}$$

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = (-6020 \text{ J mol}^{-1}) - (273.15 \text{ K})(-22.039 \text{ 172 62 J K}^{-1} \text{ mol}^{-1})$$

$$\boxed{\Delta G = 0 \text{ J mol}^{-1}}$$

b) The net heat transferred to the surroundings at the constant temperature of –10 °C :

$$-q_{\text{surr}} + q_{\text{fus}} + q_{\text{gained}} = (-753 + 6020 + 377) \text{ J mol}^{-1}$$

$$\Delta H = -q_{\text{surr}} + q_{\text{fus}} + q_{\text{gained}}$$

$$\Delta H = 5644 \text{ J mol}^{-1}$$

$$\Delta H (\text{freezing}) = -5644 \text{ J mol}^{-1}$$

$$\Delta S_{\text{sys}} = -20.64 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-5644 \text{ J mol}^{-1}) - (263.15 \text{ K})(-20.64 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\boxed{\Delta G = -212.58 \text{ J mol}^{-1}}$$

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**3.40.** At 25 °C 1 mol of an ideal gas is expanded isothermally from 2 to 20 dm<sup>3</sup>. Calculate  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$ , and  $\Delta G$ . Do the values depend on whether the process is reversible or irreversible?

**Solution:**

Given: Ideal Gas:  $n = 1$  mol,  $T = 25$  °C,  $V_i = 2$  dm<sup>3</sup>,  $V_f = 20$  dm<sup>3</sup>

Required:  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$ , and  $\Delta G$

It is important that you remember from Chapter 2 that during an isothermal compression or expansion, the change in both the internal energy and enthalpy are equal to zero due to their temperature dependence.

$$\Delta U_m = C \Delta T$$

$\Delta T = 0$  and therefore,

$$\boxed{\Delta U_m = 0}$$

$$\Delta H_m = \cancel{\Delta U_m} + \Delta(\cancel{PV})$$

$$\boxed{\Delta H_m = 0}$$

From Eq. 3.45 we are given that,

$$\Delta S_{A \rightarrow B} = \int_A^B \frac{dq_{\text{rev}}}{T}$$

The process is an isothermal expansion so the gas is being taken from state A to state B. We can now solve the integral but A and B will represent the change in volume which means that a new expression must be formulated. For an Ideal Gas, we will use Eq. 3.50;

$$q_{\text{rev}} = nRT \ln \left( \frac{V_2}{V_1} \right)$$

Since the temperature is constant, the entropy change is simply the reversible heat absorbed divided by the temperature which leads to,

$$\Delta S = nR \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S = (1 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{20}{2} \right)$$

$$\Delta S = 19.14 \text{ J K}^{-1}$$

$$\boxed{\Delta S_m = 19.14 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The equation of state (Eq. 3.86) defines the Helmholtz energy and states that:

$$A = U - TS$$

$$\Delta A = \Delta U - T \Delta S$$

Since we have already determined that the internal energy is equal to zero,

$$\Delta A = -T \Delta S$$

$$\Delta A = -(298.15 \text{ K}) (19.14 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta A = -5708 \text{ J mol}^{-1}$$

$$\boxed{\Delta A = -5.71 \text{ kJ mol}^{-1}}$$

The Gibbs energy can now be found using Eq. 3.80,

$$\Delta G = \Delta H - T \Delta S$$

Remember that the change in enthalpy is also equal to zero.

$$\Delta G = \cancel{\Delta H} - T \Delta S$$

$$\Delta G = -T \Delta S$$

$$\Delta G = -(298.15 \text{ K}) (19.14 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\boxed{\Delta G = 5.71 \text{ kJ mol}^{-1}}$$

All of the quantities calculated above are state functions. This means that the values are not determined by the way in which the process is carried out.

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**3.41.** The values of  $\Delta H$  and  $\Delta S$  for a chemical reaction are  $-85.2 \text{ kJ mol}^{-1}$  and values can be taken to be independent of temperature.

$-170.2 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, and the

**a.** Calculate  $\Delta G$  for the reaction at (a) 300 K, (b) 600 K, and (c) 1000 K.

**b.** At what temperature would  $\Delta G$  be zero?

**Solution:**

Given:  $\Delta H = -85.2 \text{ kJ mol}^{-1}$ ,  $\Delta S = -170.2 \text{ J K}^{-1}$

Required:  $\Delta G$ , at a, b, c and  $\Delta G=0$  where?

**a)** Using Eq. 3.80 at 300 K,

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-85\,200 \text{ J mol}^{-1}) - (300 \text{ K})(-170.2 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G = -34\,140 \text{ J mol}^{-1}$$

$$\boxed{\Delta G = -34.14 \text{ kJ mol}^{-1}}$$

**b)** Using Eq. 3.80 at 600 K,

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-85\,200 \text{ J mol}^{-1}) - (600 \text{ K})(-170.2 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G = 16\,920 \text{ J mol}^{-1}$$

$$\boxed{\Delta G = 16.92 \text{ kJ mol}^{-1}}$$

**c)** Using Eq. 3.80 at 1000 K,

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-85\,200 \text{ J mol}^{-1}) - (1000 \text{ K})(-170.2 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G = 85\,000 \text{ J mol}^{-1}$$

$$\boxed{\Delta G = 85.00 \text{ kJ mol}^{-1}}$$

The change in Gibbs energy will be equal to zero when,

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$\Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{-85\,200 \text{ J mol}^{-1}}{-170.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\boxed{T = 500.6 \text{ K}}$$

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- 3.42.** The standard Gibbs energy for the combustion,  $\Delta_c G^\circ$ , of methane has been measured as  $-815.04 \text{ kJ mol}^{-1}$  at  $25.0^\circ\text{C}$  and  $-802.57 \text{ kJ mol}^{-1}$  at  $75.0^\circ\text{C}$ . Assuming that Eq. 3.169 applies and that  $\Delta_c G^\circ$  changes linearly with temperature in this range, estimate the enthalpy of combustion at the midpoint of this temperature range, i.e.,  $50.0^\circ\text{C}$ .

**Solution:**

Given: methane:  $\Delta_c G^\circ = -815.04 \text{ kJ mol}^{-1}$ ,  $T = 25^\circ\text{C}$ ,  $\Delta_c G^\circ = -802.57 \text{ kJ mol}^{-1}$ ,  $T = 75^\circ\text{C}$ , Eq. 3.169

Required:  $\Delta_c H$

Eq. 3.166 gives us an important thermodynamic relationship which is called the Gibbs-Helmholtz Equation.

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p = -\frac{\Delta H}{T^2}$$

We can write,

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p = -\frac{\Delta H}{T^2}$$

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p \approx \frac{1}{T_2 - T_1} \left( \frac{\Delta_c G_2^\circ}{T_2} - \frac{\Delta_c G_1^\circ}{T_1} \right) = -\frac{\Delta_c H^\circ}{T^2}$$

$T$  is the midpoint of the temperature range ( $50.0^\circ\text{C}$ ). In the limit  $\Delta T \rightarrow 0$  we will obtain the following;

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p \approx \frac{1}{T_2 - T_1} \left( \frac{\Delta_c G_2^\circ}{T_2} - \frac{\Delta_c G_1^\circ}{T_1} \right) = -\frac{\Delta_c H^\circ}{T^2}$$

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p \approx \frac{1}{348.0 \text{ K} - 298.0 \text{ K}} \left( \frac{-802.57 \text{ kJ mol}^{-1}}{348.0 \text{ K}} - \frac{-815.04 \text{ kJ mol}^{-1}}{298.0 \text{ K}} \right)$$

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p \approx 8.576 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} = -\frac{\Delta_c H^\circ}{T^2}$$

$$\Delta_c H^\circ = -\left( 8.576 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \right) T^2$$

$$\Delta_c H^\circ = -\left( 8.576 \times 10^{-3} \text{ kJ } \cancel{\text{K}}^{-1} \text{ mol}^{-1} \right) \left( 323.0 \cancel{\text{K}} \right)^2$$

$$\boxed{\Delta_c H^\circ = -894.72 \text{ kJ mol}^{-1}}$$

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**3.43.** The heat of vaporization of water at 25 °C is 44.01 kJ mol<sup>-1</sup>, and the equilibrium vapor pressure at that temperature is 0.0313 atm. Calculate  $\Delta S$ ,  $\Delta H$ , and  $\Delta G$  when 1 mol of liquid water at 25 °C is converted into vapor at 25 °C and a pressure of 10<sup>-5</sup> atm, assuming the vapor to behave ideally.

**Solution:**

Given:  $\Delta_{\text{vap}} H_{\text{water}} = 44.01 \text{ kJ mol}^{-1}$ ,  $T = 25 \text{ }^{\circ}\text{C}$ ,  $P_{\text{eq}} = 0.0313 \text{ atm}$ ,  $n_{\text{water}} = 1 \text{ mol}$ ,  $P = 10^{-5} \text{ atm}$

Required:  $\Delta S$ ,  $\Delta H$ , and  $\Delta G$

For the conversion of water to vapor at 25 °C and 0.0313 atm,

$$\boxed{\Delta H_{\text{vap}}(\text{water}) = 44.01 \text{ kJ mol}^{-1}}$$

$$\Delta S = \frac{q_{\text{vap}}}{T} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\Delta S = \frac{44\,010 \text{ J mol}^{-1}}{298.15 \text{ K}}$$

$$\Delta S = 147.610\,263\,3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S = 147.61 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (44\,010 \text{ J mol}^{-1}) - (298.15 \text{ K})(147.610\,263\,3 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\boxed{\Delta G = 0}$$

However, under a reversible isothermal expansion from 0.0313 atm to 10<sup>-5</sup> atm we will obtain,

$$\boxed{\Delta H = 0}$$

$$\Delta S_{\text{rev}} = \int_A^B \frac{dq_{\text{vap}}}{T}$$

$$q = nRT \ln \left( \frac{P_1}{P_2} \right)$$

$$\Delta S_{\text{rev}} = R \ln \left( \frac{P_1}{P_2} \right)$$

$$\Delta S_{\text{rev}} = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{0.0313}{10^{-5}} \right)$$

$$\Delta S_{\text{rev}} = 66.921 \ 650 \ 18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_{\text{rev}} = 66.9 \text{ J K}^{-1} \text{ mol}^{-1}}$$

However, for the entire entropy change in the system, we will have to add up the last two entropies calculated to get,

$$\Delta S_{\text{tot}} = (66.921 \ 650 \ 18 \text{ J K}^{-1} \text{ mol}^{-1}) + (147.610 \ 263 \ 3 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta S_{\text{tot}} = 214.531 \ 913 \ 5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_{\text{tot}} = 214.5 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = (44 \ 010 \text{ J mol}^{-1}) - (298.15 \text{ K})(214.531 \ 913 \ 5 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G = -19 \ 952.690 \ 01 \text{ J mol}^{-1}$$

$$\boxed{\Delta G = -19.95 \text{ kJ mol}^{-1}}$$

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**3.44.** For each of the following processes, state which of the quantities  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$  and  $\Delta G$  are equal to zero:

- a. Isothermal reversible expansion of an ideal gas.
- b. Adiabatic reversible expansion of a nonideal gas.
- c. Adiabatic expansion of an ideal gas through a throttling valve.
- d. Adiabatic expansion of a nonideal gas through a throttling valve.
- e. Vaporization of liquid water at 80 °C and 1 bar pressure.
- f. Vaporization of liquid water at 100 °C and 1 bar pressure.
- g. Reaction between  $\text{H}_2$  and  $\text{O}_2$  in a thermally insulated bomb.
- h. Reaction between  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  in dilute aqueous solution at constant temperature and pressure.

**Solution:**

Given: see above

Required:  $U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$  and  $\Delta G$  are equal to zero where?

a. Isothermal reversible expansion of an ideal gas

→  $\Delta U$  and  $\Delta H$  since they are temperature dependent and if there is no change in temperature, then they must be equal to zero.

b. Adiabatic reversible expansion of a nonideal gas.

→  $\Delta S$  will be equal to zero due to the nature of the expansion.

c. Adiabatic expansion of an ideal gas through a throttling valve.

→  $\Delta H$  will be equal to zero

d. Adiabatic expansion of a nonideal gas through a throttling valve.

→  $\Delta H$  will be equal to zero

e. Vaporization of liquid water at 80 °C and 1 bar pressure.

None of the above will be equal to zero.

f. Vaporization of liquid water at 100 °C and 1 bar pressure.

→  $\Delta G$  due to the fact that here, the system will be at equilibrium

**g.** Reaction between  $\text{H}_2$  and  $\text{O}_2$  in a thermally insulated bomb.

→  $\Delta U$  will be equal to zero

**h.** Reaction between  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  in dilute aqueous solution at constant temperature and pressure.

None of the above will be equal to zero.

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**3.45.** Calculate the change  $\Delta G_m$  in the Gibbs energy of 1 mol of liquid mercury initially at 1 bar pressure if a pressure of 1000 bar is applied to it. The process occurs at the constant temperature of 25 °C, and the mercury may be assumed to be incompressible and to have a density of 13.5 g cm<sup>-3</sup>.

**Solution:**

Given:  $n_{\text{Hg}} = 1 \text{ mol}$ ,  $P_i = 1 \text{ bar}$ ,  $P_{\text{ext}} = 1000 \text{ bar}$ ,  $T = 25 \text{ °C}$ ,  $\rho_{\text{Hg}} = 13.5 \text{ g cm}^{-3}$

Required:  $\Delta G_m$

Eq. 3.154 states that,

$$dG = V_m dP$$

This means that under the isothermal conditions, we can write;

$$\left( \frac{\partial G}{\partial P} \right)_T = V$$

$$\Delta G = \int V dP$$

$$\Delta G_m = \int_{P_i}^{P_{\text{ext}}} V_m dP = V_m \Big|_{P_i}^{P_{\text{ext}}}$$

$$\Delta G_m = V_m (P_{\text{ext}} - P_i)$$

$$\Delta G_m = V_m (P_{\text{ext}} - P_i)$$

We must first determine the molar volume for the liquid mercury. Since we are given the density, this can be easily determined.

$$\rho_{\text{Hg}} = 13.5 \text{ g cm}^{-3}$$

$$\rho_{\text{Hg}} = \frac{m}{V}$$

$$m = nM$$

$$V_m = \frac{M}{\rho_{\text{Hg}}} = \frac{(200.6 \text{ g mol}^{-1})}{(13.5 \text{ g cm}^{-3})}$$

$$V_m = 14.859 \text{ 259 cm}^3 \text{ mol}^{-1}$$

$$\text{since } 1 \text{ cm}^3 = 1.0 \times 10^{-6} \text{ m}^3$$

$$V_m = 14.859 \text{ 259 } \cancel{\text{cm}^3} \text{ mol}^{-1} \times \frac{1.0 \times 10^{-6} \text{ m}^3}{\cancel{1 \text{ cm}^3}}$$

$$V_m = 1.486 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Now substituting all the appropriate values into the expression derived above we obtain,

$$\Delta G_m = V_m (P_{\text{ext}} - P_i)$$

$$\Delta G_m = (1.486 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})(1000 - 1) \text{ bar}$$

$$\Delta G_m = (1.486 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})(999 \text{ bar})$$

$$\Delta G_m = 0.014 \text{ 844 4 m}^3 \text{ bar mol}^{-1}$$

$$1 \text{ bar} = 10^5 \text{ Pa}, 1 \text{ Pa m}^3 = 1 \text{ J}$$

$$\Delta G_m = (0.014 \text{ 844 4 m}^3 \cancel{\text{bar}} \text{ mol}^{-1})(10^5 \text{ Pa } \cancel{\text{bar}^{-1}})$$

$$\Delta G_m = 1 \text{ 484.44 Pa m}^3 \text{ mol}^{-1}$$

$$\Delta G_m = 1 \text{ 484.44 J mol}^{-1}$$

$$\boxed{\Delta G_m = 1.485 \text{ kJ mol}^{-1}}$$

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**3.46.** The entropy of argon is given to a good approximation by the expression

$$S_m / \text{J K}^{-1} \text{ mol}^{-1} = 36.36 + 20.79 \ln(T/\text{K})$$

Calculate the change in Gibbs energy of 1 mol of argon if it is heated at constant pressure from 25 °C to 50 °C.

**Solution:**

Given:  $S_m / \text{J K}^{-1} \text{ mol}^{-1} = 36.36 + 20.79 \ln(T/\text{K})$

$$n_{\text{argon}} = 1 \text{ mol}, T_i = 25 \text{ }^\circ\text{C}, T_f = 50 \text{ }^\circ\text{C}$$

Required:  $\Delta G$

Just like in the previous problem which dealt with mercury at constant temperature, we will begin by defining the Gibbs energy as a partial differential. Eq. 3.161 describes Gibbs energy at constant pressure.

$$\left( \frac{\partial G_m}{\partial T} \right)_P = -S_m$$

Since we have been given an approximation for entropy, let us say:

$$S_m / \text{J K}^{-1} \text{ mol}^{-1} = 36.36 + 20.79 \ln(T / \text{K})$$

$$A = 36.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$B = 20.79 \text{ J K}^{-1} \text{ mol}^{-1}$$

We can now take the integral of both side of Eq. 3.161 in order to obtain,

$$\left(\frac{\partial G_m}{\partial T}\right)_P = -S_m$$

$$\Delta G_m = \int -S_m dT$$

$$\Delta G_m = -\int_{298.15}^{323.15} (A + B \ln T) dT$$

$$\Delta G_m = -\left[AT + B(T \ln T - T)\right] \Big|_{298.15}^{323.15}$$

$$\Delta G_m = -\left[AT + BT \ln T - BT\right] \Big|_{298.15}^{323.15}$$

$$\Delta G_m = -AT - BT \ln T + BT \Big|_{298.15}^{323.15}$$

$$\Delta G_m = -(A - B)T - BT \ln T \Big|_{298.15}^{323.15}$$

$$\begin{aligned} \Delta G_m = & -(36.36 - 20.79) \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1} \times (323.15 - 298.15) \cancel{\text{K}} \\ & - \left(20.79 \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1}\right) \left(323.15 \times \ln(323.15) - 298.15 \times \ln(298.15)\right) \cancel{\text{K}} \end{aligned}$$

$$\Delta G_m = -389.25 \text{ J mol}^{-1} - 3\,502.281\,785 \text{ J mol}^{-1}$$

$$\Delta G_m = -3\,891.531\,785 \text{ J mol}^{-1}$$

$$\boxed{\Delta G_m = -3.89 \text{ kJ mol}^{-1}}$$

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- 3.47.** Calculate the absolute entropy of  $\text{SO}_2(\text{g})$  at 300.0 K and 1 bar given the following information:  $S^\circ(15.0 \text{ K}) = 1.26 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $C_{P,m}(\text{s}) = 32.65 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T_{\text{fus}} = 197.64 \text{ K}$ ,  $\Delta_{\text{fus}}H^\circ = 7\,402 \text{ J mol}^{-1}$ ,  $C_{P,m}(\text{l}) = 87.20 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T_{\text{vap}} = 263.08 \text{ K}$ ,  $\Delta_{\text{vap}}H^\circ = 24\,937 \text{ J mol}^{-1}$ ,  $C_{P,m}(\text{g}) = 39.88 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Solution:**

Given: see above

Required:  $\Delta S_{\text{abs}}$

The absolute entropy of  $\text{SO}_2(\text{g})$  at 300.0 K and 1 bar can be calculated using the following:

$$S^\circ(300 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = S^\circ(15.0 \text{ K}) + \int_{15.0 \text{ K}}^{T_{\text{fus}}} \frac{C_{P,m}(\text{s})}{T} dT + \frac{\Delta_{\text{fus}}H^\circ}{T} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_{P,m}(\text{l})}{T} dT \\ + \frac{\Delta_{\text{vap}}H^\circ}{T} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_{P,m}(\text{g})}{T} dT$$

Now we can simply substitute all of the values given in the problem into the equation stated above. Since we are asking for the absolute entropy of this compound in the gaseous phase, we must consider the changes that accompany each phase that comes before it. This is why all of the information given above is important.

$$S^\circ(300.0 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 1.26 + \int_{15.0}^{197.64} \frac{32.65}{T} dT + \frac{7\,402}{197.64} + \int_{197.64}^{263.08} \frac{87.20}{T} dT \\ + \frac{24\,937}{263.08} + \int_{263.08}^{300.0} \frac{39.88}{T} dT$$

$$S^\circ(300.0 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 1.26 + 32.65 \times \ln\left(\frac{197.64}{15.0}\right) + 37.451\,932\,81 + 87.20 \times \ln\left(\frac{263.08}{197.64}\right) \\ + 94.788\,657\,44 + 39.88 \times \ln\left(\frac{300.0}{263.08}\right)$$

$$S^\circ(300.0 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 1.26 + 84.184\,661\,82 + 37.451\,932\,81 + 24.940\,156\,97 \\ + 94.788\,657\,44 + 5.237\,213\,332$$

$$S^\circ(300.0 \text{ K}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 247.862\,622\,4$$

$$\boxed{S^\circ(300.0 \text{ K}) = 247.86 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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- 3.48.** Initially at 300 K and 1 bar pressure, 1 mol of an ideal gas undergoes an irreversible isothermal expansion in which its volume is doubled, and the work it performs is  $500 \text{ J mol}^{-1}$ . What are the values of  $q$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$ ? What would  $q$  and  $w$  be if the expansion occurred reversibly?

**Solution:**

Given: Ideal Gas:  $n = 1 \text{ mol}$ ,  $P = 1 \text{ bar}$ ,  $T = 300 \text{ K}$ ,  $\Delta V = 2$ ,  $w = 500 \text{ J mol}^{-1}$

Required:  $q$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  and  $q$  &  $w$  (reversible)

Under the irreversible isothermal conditions:

Remember that we have seen numerous times that  $\Delta U$  and  $\Delta H$  are equal to zero due to the fact that  $\Delta U = C_v \Delta T$  and  $\Delta H = C_p \Delta T$ . Since they are dependent on temperature change, it is obvious that these will be equal to zero under isothermal conditions whether they be reversible or irreversible.

$$\boxed{\Delta U = 0}$$

$$\boxed{\Delta H = 0}$$

From the equation which describes the change in internal energy, we can determine the work and heat.

$$\Delta U = w + q$$

$$\Delta U = 0 \text{ therefore,}$$

$$q = -w$$

$$\boxed{q = 500 \text{ J mol}^{-1}}$$

Remember to read carefully and understand that the system is doing work and therefore, that would mean that the value they give us should actually have the opposite sign. This is why the heat has a positive value.

$$\Delta S = \int \frac{dq}{T}$$

$$q = nRT \ln V$$

For a single mole and at constant temperature this expression comes down to,

$$\Delta S = \int \frac{dq}{T}$$

$$q = nRT \ln V$$

$$\Delta S = R \ln V \Big|_{V_1}^{V_2}$$

$$\Delta S = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(2)$$

$$\boxed{\Delta S = 5.763 \text{ J K}^{-1} \text{ mol}^{-1}}$$

With all of the above information we are now able to calculate the change in Gibbs energy according to Eq. 3.80.

$$G = H - TS$$

$$\Delta G = \cancel{\Delta H} - T \Delta S$$

$$\Delta H = 0$$

$$\Delta G = -T \Delta S$$

$$\Delta G = -(300 \text{ K})(5.736 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G = -1728.95 \text{ J mol}^{-1}$$

$$\boxed{\Delta G = -1.73 \text{ kJ mol}^{-1}}$$

Under reversible conditions, we can assume the following;

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + w_{\text{rev}}$$

$$\Delta G = \Delta H - T \Delta S \rightarrow \Delta H = \Delta G + T \Delta S$$

$$\cancel{\Delta G} + T \Delta S = \cancel{\Delta U} + w_{\text{rev}}$$

$$w_{\text{rev}} = T \Delta S$$

$$\boxed{w_{\text{rev}} = 1.73 \text{ kJ mol}^{-1}}$$

And using the expression we originally found between work and heat,

$$w_{\text{rev}} = 1.73 \text{ kJ mol}^{-1}$$

$$q_{\text{rev}} = -w_{\text{rev}}$$

$$q_{\text{rev}} = -1.73 \text{ kJ mol}^{-1}$$

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**\*3.49.** At 100 °C 1 mol of liquid water is allowed to expand isothermally into an evacuated vessel of such a volume that the final pressure is 0.5 atm. The amount of heat absorbed in the process was found to be 30 kJ mol<sup>-1</sup>. What are  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ ?

**Solution:**

Given:  $n_{\text{water}} = 1 \text{ mol}$ ,  $T = 100 \text{ °C}$ ,  $P_i = 0$ ,  $P_f = 0.5 \text{ atm}$ ,  $q = 30 \text{ kJ mol}^{-1}$

Required:  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$

In an evacuated vessel,  $P_{\text{ext}} = 0$ , which implies that no work is done.

$$\boxed{w = 0}$$

We can use a very familiar equation from Chapter 2 to determine the change in internal energy.

$$\Delta U = w + q$$

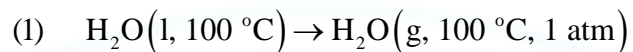
since  $w = 0$  then,

$$\Delta U = q$$

$$\boxed{\Delta U = 30 \text{ kJ mol}^{-1}}$$

At 100 °C, liquid water will begin to go into the vapor phase. When we are working under these conditions, we can make the following approximation:





$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta(PV) = \Delta nRT$$

$$\Delta H = \Delta U + \Delta nRT$$

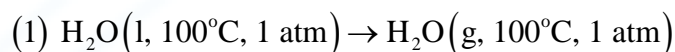
$$\Delta n = 1$$

$$\Delta H = (30\,000 \text{ J mol}^{-1}) + (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K})$$

$$\Delta H = 33\,102.555 \text{ J mol}^{-1}$$

$$\boxed{\Delta H = 33.10 \text{ kJ mol}^{-1}}$$

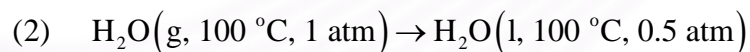
In order to determine the change in entropy, we should consider this process to be both isothermal and reversible. This will enable us to use the following expression:



$$\Delta S_1(\text{evaporation}) = \frac{\Delta H_{\text{fus}}}{T}$$

$$\Delta S_1(\text{evaporation}) = \frac{40\,600 \text{ J mol}^{-1}}{373.15 \text{ K}}$$

$$\Delta S_1(\text{evaporation}) = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}$$



$$\Delta S_2 = \int \frac{q_{\text{rev}}}{T}$$

$$q_{\text{rev}} = nRT \ln V$$

$$\Delta S_2 = R \ln \frac{V_2}{V_1}$$

$$\Delta S_2 = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(2)$$

$$\Delta S_2 = 5.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

Since the pressure is decreasing by one half, it would follow that the volume would double during the process, this is why we are not directly using the pressure values. Now we can determine the net change in entropy.

$$\Delta S_{\text{net}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_{\text{net}} = (108.8 + 5.76) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_{\text{net}} = 114.6 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The Gibbs energy can be found according to Eq. 3.80:

$$G = H - TS$$

$$\Delta G = \Delta H - T \Delta S$$

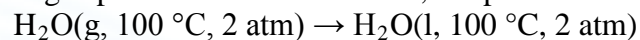
$$\Delta G = (33\,100 \text{ J mol}^{-1}) - (373.15 \text{ K})(86.16 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\boxed{\Delta G = 949.396 \text{ J mol}^{-1}}$$

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**\*3.50.** Water vapor can be maintained at 100 °C and 2 atm pressure for a time, but it is in a state of metastable equilibrium and is said to be supersaturated. Such a system will undergo spontaneous condensation; the process is:



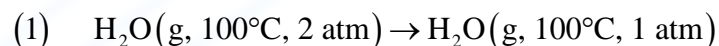
Calculate  $\Delta H_m$ ,  $\Delta S_m$ , and  $\Delta G_m$ . The molar enthalpy of vaporization  $\Delta_{\text{vap}}H_m$  is 40.60 kJ mol<sup>-1</sup>; assume the vapor to behave ideally and liquid water to be incompressible.

**Solution:**

Given: see above

Required:  $\Delta H_m$ ,  $\Delta S_m$ , and  $\Delta G_m$

In order to solve this problem, we must break down the process into three distinct and reversible steps.



$$\Delta H_1 = 0$$

$$\Delta S_1 = R \ln \frac{V_2}{V_1} \quad (\text{Eq. 3.94})$$

$$\Delta S_1 = (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \ln \frac{2\text{ atm}}{1\text{ atm}}$$

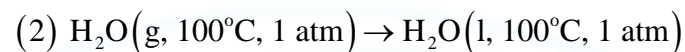
$$\Delta S_1 = 5.763\,172\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta G_1 = \cancel{\Delta H_1} - T\Delta S_1$$

$$\Delta G_1 = -(373.15\text{ K})(5.763\,172\text{ J K}^{-1}\text{ mol}^{-1})$$

$$\Delta G_1 = -2150\text{ J mol}^{-1}$$

Recall that for an isothermal process, there is no change in enthalpy.



$$\Delta H_2 = -\Delta_{\text{vap}} H_m = -40\,600 \text{ J mol}^{-1}$$

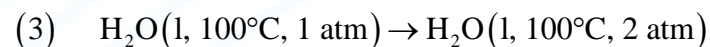
$$\Delta S_2 (\text{condensation}) = -\frac{\Delta_{\text{vap}} H_m}{T}$$

$$\Delta S_2 (\text{condensation}) = -\frac{40\,600 \text{ J mol}^{-1}}{373.15 \text{ K}}$$

$$\Delta S_2 (\text{condensation}) = -108.803\,430 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G_2 = 0$$

For a reversible process at constant  $T$  and  $P$ , there is no change in Gibbs energy.



The enthalpy, entropy and Gibbs energy changes are negligible for this particular step of the process. We can now sum up all of the values in order to determine the  $\Delta H_m$ ,  $\Delta S_m$ , and  $\Delta G_m$ .

$$\Delta H_m = \cancel{\Delta H_1} + \Delta H_2 + \cancel{\Delta H_3}$$

$$\boxed{\Delta H_m = -40.6 \text{ kJ}}$$

$$\Delta S_m = (5.763\,172 - 108.803\,430 + \cancel{\Delta S_3}) \text{ J K}^{-1}$$

$$\boxed{\Delta S_m = -103 \text{ J K}^{-1}}$$

$$\Delta G_m = \Delta G_1 + \cancel{\Delta G_2} + \cancel{\Delta G_3}$$

$$\Delta G_m = -2150 \text{ J}$$

$$\boxed{\Delta G_m = -2.15 \text{ kJ}}$$

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**\*3.51.** Initially at 300 K and 10 atm pressure, 1 mol of a gas is allowed to expand adiabatically against a constant pressure of 4 atm until equilibrium is reached. Assume the gas to be ideal with:

$$C_{P,m}/\text{J K}^{-1} \text{ mol}^{-1} = 28.58 + 1.76 \times 10^{-2} T/\text{K}$$

and calculate  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$ .

**Solution:**

Given:  $T_i = 300 \text{ K}$ ,  $P_i = 10 \text{ atm}$ ,  $n = 1 \text{ mol}$ ,  $P_f = 4 \text{ atm}$

Required:  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$

Remember from Chapter 2, that an adiabatic process is one that occurs in a vessel whose walls are perfectly insulating so that no heat can pass through them. In short, there is no heat exchange between the system and the surroundings. Normally, we know that,  $dU = dq - PdV$  however, since  $dq = 0$  then we can determine the change in internal energy according to the following:

$$\Delta U = \int_{T_i}^{T_f} C_{V,m} dT$$

$$C_{P,m} - C_{V,m} = R$$

$$C_{V,m} = C_{P,m} - R$$

$$C_{V,m} = \left[ (28.58 + 1.76 \times 10^{-2} T / \text{K}) - 8.3145 \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{V,m} = (20.2655 + 1.76 \times 10^{-2} T / \text{K}) \text{ J K}^{-1} \text{ mol}^{-1}$$

Since we have only been given the initial temperature, we can rearrange the expression using Eq. 2.81 in order to make use of the pressure values stated above.

$$nC_{V,m}dT + PdV = 0$$

$$(1 \text{ mol})C_{V,m}dT = -P_f dV = dw$$

$$\Delta U_m = \int_{T_i}^{T_f} (20.2655 + 1.76 \times 10^{-2} T / \text{K}) dT$$

$$\Delta U_m = -\int_{V_i}^{V_f} P_f dV$$

$$\Delta U_m = -P_f \int_{V_i}^{V_f} dV$$

Assuming that the gas is ideal, we can use the Ideal Gas Law in order to finish solving this integration.

$$PV = nRT$$

$$V_i = \cancel{n} \frac{RT_i}{P_i}, V_f = \cancel{n} \frac{RT_f}{P_f}$$

$$\Delta U_m = -P_f \left( \frac{RT_f}{P_f} - \frac{RT_i}{P_i} \right)$$

$$\Delta U_m = -4 \text{ atm} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \left( \frac{T_f}{4 \text{ atm}} - \frac{300 \text{ K}}{10 \text{ atm}} \right)$$

$$\Delta U_m = -4 \text{ atm} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \left( \frac{T_f}{4 \text{ atm}} - \frac{30 \text{ K}}{1 \text{ atm}} \right)$$

Now we can use the initial expression found for the change in internal energy. We can set both equations equal to one another in order to solve for the final temperature.

$$\Delta U_m = \int_{T_i}^{T_f} (20.2655 + 1.76 \times 10^{-2} T / \text{K}) dT$$

$$\Delta U_m = 20.2655(T_f - T_i) + \frac{1}{2} 1.76 \times 10^{-2} (T_f^2 - T_i^2)$$

$$\Delta U_m = 20.2655(T_f - 300) + 0.00898(T_f^2 - 300^2)$$

$$20.2655(T_f - 300) + 0.00898(T_f^2 - 300^2) = -4 \cancel{\text{ atm}} \times 8.3145 \text{ J } \cancel{\text{ K}^{-1}} \text{ mol}^{-1} \left( \frac{T_f}{\cancel{4 \text{ atm}}} - \frac{30 \cancel{\text{ K}}}{1 \cancel{\text{ atm}}} \right)$$

$$20.2655T_f - 6079.65 + 0.00898T_f^2 - 808.2 = -8.3145T_f + 997.74$$

$$0.00898T_f^2 + 28.58T_f - 7885.59 = 0$$

This can be solved using the quadratic equation.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$T_f = \frac{-28.58 \pm \sqrt{28.58^2 - 4 \times 0.008\,98 \times (-7\,885.59)}}{2 \times 0.008\,98}$$

$$T_f = \frac{-28.58 \pm 33.167\,254\,83}{0.017\,96}$$

taking the positive root,

$$T_f = 255.415\,079\,6\,\text{K}$$

$$\Delta U_m = 20.2655(255.415\,079\,6 - 300) + 0.008\,98(255.415\,079\,6^2 - 300^2)$$

$$\Delta U_m = -1\,125.908\,676\,\text{J mol}^{-1}$$

$$\boxed{\Delta U_m = -1\,125.9\,\text{J mol}^{-1}}$$

$$\Delta H_m = 28.58(255.415\,079\,6 - 300) + 0.008\,98(255.415\,079\,6^2 - 300^2)$$

$$\Delta H_m = -1496.609\,996\,\text{J mol}^{-1}$$

$$\boxed{\Delta H_m = -1496.6\,\text{J mol}^{-1}}$$

For 1 mol of ideal gas,  $PV_m = RT$

$$d(PV_m) = RdT = PdV_m + V_mdP$$

$$PdV_m = RdT - V_mdP = RdT - \frac{RT}{P}dP$$

$$dS_m = \frac{dU_m + RdT - \frac{RTdP}{P}}{T} = \frac{C_{P,m}}{T}dT - \frac{R}{P}dP$$

$$\Delta S_m / \text{J K}^{-1} \text{ mol}^{-1} = \int_{300}^{255.3} \frac{28.58 + 0.0176T}{T} dT - 8.3145 \ln\left(\frac{4}{10}\right)$$

$$\Delta S_m / \text{J K}^{-1} \text{ mol}^{-1} = 28.58 \ln\left(\frac{255.3}{300}\right) + 0.0176(255.3 - 300) + 7.618 \ 499 \ 29$$

$$\Delta S_m / \text{J K}^{-1} \text{ mol}^{-1} = 2.220 \ 592 \ 051$$

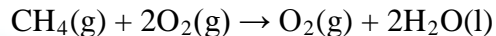
$$\boxed{\Delta S_m = 2.22 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.52.** Calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  for the reaction



making use of the data in Appendix D.

**Solution:**

Given: Appendix D

Required:  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$

It is possible to use the enthalpies and free energies of formation in conjunction with a form of Eq. 2.53 in order to solve for the standard enthalpy and standard Gibbs energy for the reaction given above. Recall that all of the values given in Appendix D were taken at 298.15 K.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = 2\Delta_f H^\circ(\text{H}_2\text{O}, \text{l}) - \left[ \Delta_f H^\circ(\text{CH}_4, \text{g}) + 2\cancel{\Delta_f H^\circ(\text{O}_2, \text{g})} \right]$$

$$\Delta H^\circ = \left[ (2 \times -285.830) - (-74.6) \right] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -497 \text{ kJ mol}^{-1}}$$

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = 2\Delta_f G^\circ(\text{H}_2\text{O}, \text{l}) - \left[ \Delta_f G^\circ(\text{CH}_4, \text{g}) + 2\cancel{\Delta_f G^\circ(\text{O}_2, \text{g})} \right]$$

$$\Delta G^\circ = \left[ (2 \times -237.1) - (-50.5) \right] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G^\circ = -424 \text{ kJ mol}^{-1}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{(-497 + 424) \text{ kJ mol}^{-1}}{298.15 \text{ K}}$$

$$\boxed{\Delta S^\circ = -245 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**3.53.** The following is a set of special conditions:

- a. True only for an ideal gas.
- b. True only for a reversible process.
- c. True only if  $S$  is the total entropy (system + surroundings).
- d. True only for an isothermal process occurring at constant pressure.
- e. True only for an isothermal process occurring at constant volume.

Consider each of the following statements, and indicate which of the above conditions must apply in order for the statement to be true:

- a.  $\Delta U = 0$  for an isothermal process.
- b.  $\Delta H = 0$  for an isothermal process.
- c. The total  $\Delta S = 0$  for an adiabatic process.
- d.  $\Delta S >$  ☐ 0 for a spontaneous process.
- e.  $\Delta G <$  ☐ 0 for a spontaneous process.

**Solution:**

- a)  $\Delta U = 0$  for an isothermal process only when the gas is an *Ideal Gas*
- b)  $\Delta H = 0$  for an isothermal process only when the gas is an *Ideal Gas*
- c) The total  $\Delta S = 0$  for an adiabatic process when this *process is a reversible one*
- d)  $\Delta S >$  ☒ 0 if entropy change is occurring in the system considering the *total entropy change occurring in the system*
- e)  $\Delta G <$  ☐ 0 for a spontaneous process

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**3.54.** Calculate the entropy and Gibbs energy changes for the conversion of 1 mol of liquid water at 100 °C and 1 bar pressure into vapor at the same temperature and a pressure of 0.1 bar. Assume ideal behavior. The heat of vaporization of water at 100 °C is 40.6 kJ mol<sup>-1</sup>.

**Solution:**

Given:  $n_{\text{water}} = 1 \text{ mol}$ ,  $T = 100^\circ\text{C}$ ,  $P_{\text{water}} = 1 \text{ bar}$ ,  $P_{\text{vap}} = 0.1 \text{ bar}$ ,  $\Delta_{\text{vap}}H_{\text{water}} = 40.6 \text{ kJ mol}^{-1}$

Required:  $\Delta S$ ,  $\Delta G$

There are two stages to this process. First we must determine the entropy change when heating the liquid water to bring it to the vapor phase. After this, we must expand the gas from the initial pressure to the final pressure of 0.1 bar. This will yield the following:

(1) Vaporize water at 1 bar

$$\Delta S_1 = \frac{\Delta_{\text{vap}}H_m}{T}$$

$$\Delta S_1 = \frac{40\,600 \text{ J mol}^{-1}}{373.15 \text{ K}}$$

$$\Delta S_1 = 108.803\,430 \text{ J K}^{-1} \text{ mol}^{-1}$$

(2) Expansion from 1 bar to 0.1 bar

$$\Delta S_2 = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}$$

$$\Delta S_2 = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{1}{0.1}$$

$$\Delta S_2 = 19.144\,844 \text{ J K}^{-1} \text{ mol}^{-1}$$

The net entropy change is therefore;

$$\Delta S_{\text{net}} = \Delta S_1 + \Delta S_2$$

$$\boxed{\Delta S_{\text{net}} = 127.9 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 40\,600 \text{ J mol}^{-1} - (373.15 \text{ K} \times 127.9 \text{ J K}^{-1} \text{ mol}^{-1})$$

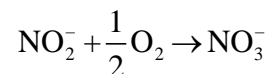
$$\Delta G = -7143.898 \text{ J mol}^{-1}$$

$$\boxed{\Delta G = -7.144 \text{ kJ mol}^{-1}}$$

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**3.55.** In the bacterium *nitrobacter* the following reaction occurs:



Use the data in Appendix D to calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  for the reaction.

**Solution:**

Given: Appendix D

Required:  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$

We will use the same method as previously done for this type of question.

$$\Delta H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants}) \quad \Delta H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

$$\Delta H^\circ = \Delta_f H^\circ (\text{NO}_3^-) - \Delta_f H^\circ (\text{NO}_2^-)$$

$$\Delta G^\circ = \Delta_f G^\circ (\text{NO}_3^-) - \Delta_f G^\circ (\text{NO}_2^-)$$

$$\Delta H^\circ = (-206.85 + 104.6) \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = (-108.74 + 32.2) \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -102.25 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -76.54 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -102.3 \text{ kJ mol}^{-1}}$$

$$\boxed{\Delta G^\circ = -76.5 \text{ kJ mol}^{-1}}$$

$$\Delta H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$T \Delta S^\circ = \Delta H^\circ - \Delta G^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{(-102.3 - (-76.5)) \text{ kJ mol}^{-1}}{298.15 \text{ K}}$$

$$\Delta S^\circ = -0.086533624 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ = -86.5 \text{ J mol}^{-1}}$$

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**3.56.** At 100 atm pressure water boils at 312 °C, while at 5 atm it boils at 152 °C. Compare the Carnot efficiencies of 100-atm and 5-atm steam engines, if  $T_c$  is 30 °C.

**Solution:**

Given: water:  $P_1 = 100$  atm,  $T_1 = 312$  °C,  $P_2 = 5$  atm,  $T_2 = 152$  °C,  $T_c = 30$  °C

Required: Carnot efficiencies for steam engines

Recall that the efficiency is given by Eq. 3.21 which states:

$$e = \frac{T_h - T_c}{T_h}$$

For the 100-atm steam engine:

$$T_h = 585.15 \text{ K}, T_c = 303.15 \text{ K}$$

$$e = \frac{(585.15 - 303.15) \cancel{\text{K}}}{585.15 \cancel{\text{K}}}$$

$$e = 0.48$$

$$\boxed{e = 48\%}$$

For the 5-atm steam engine:

$$T_h = 425.15 \text{ K}, T_c = 303.15 \text{ K}$$

$$e = \frac{(425.15 - 303.15) \cancel{\text{K}}}{425.15 \cancel{\text{K}}}$$

$$e = 0.29$$

$$\boxed{e = 29\%}$$

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**3.57.** A cooling system is designed to maintain a refrigerator at  $-4\text{ }^{\circ}\text{C}$  in a room at  $20\text{ }^{\circ}\text{C}$ . If  $10^4\text{ J}$  of heat leaks into the refrigerator each minute, and the system works at 40% of its maximum thermodynamic efficiency, what is the power requirement in watts? [1 watt (W) =  $1\text{ J s}^{-1}$ .]

**Solution:**

Given:  $T_{\text{system}} = -4\text{ }^{\circ}\text{C}$ ,  $T_{\text{room}} = 20\text{ }^{\circ}\text{C}$ ,  $q = 10^4\text{ J min}^{-1}$

Required:  $P(40\%)$

Eq. 3.21 gives the efficiency for this cooling system.

$$e = \frac{T_h - T_c}{T_h}$$

$$e = \frac{T_{\text{room}} - T_{\text{system}}}{T_{\text{room}}}$$

$$e = \frac{(293.15 - 269.15)\text{ K}}{293.15\text{ K}}$$

$$e = 0.082$$

$$e = \frac{w}{q_c} = \frac{T_h - T_c}{T_h}$$

$$w = eq_c = (0.082)(10^4)\text{ J min}^{-1}$$

$$w = 818.69\text{ J min}^{-1}$$

$$w = 818.69 \text{ J } \cancel{\text{min}^{-1}} \times \frac{1 \cancel{\text{min}}}{60 \text{ sec}}$$

$$w = 13.64 \text{ J s}^{-1}$$

$$P(40\%) = \frac{w}{e}$$

$$P(40\%) = \frac{13.64 \text{ J s}^{-1}}{0.4}$$

$$\boxed{P(40\%) = 34.1 \text{ W}}$$

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**3.58.** A heat pump is employed to maintain the temperature of a house at 25 °C. Calculate the maximum performance factor of the pump when the external temperature is (a) 20 °C, (b) 0 °C, and (c) -20 °C.

**Solution:**

Given:  $T_{\text{house}} = 25\text{ °C}$

Required: performance factor for a, b, c

**a)** at 20 °C;

$$Pf = \frac{1}{e}$$

$$Pf = \frac{T_h}{T_h - T_c}$$

$$Pf = \frac{298.15\text{ K}}{(298.15 - 293.15)\text{ K}}$$

$$\boxed{Pf = 59.63\%}$$

**b)** at 0 °C;

$$Pf = \frac{1}{e}$$

$$Pf = \frac{T_h}{T_h - T_c}$$

$$Pf = \frac{298.15\text{ K}}{(298.15 - 273.15)\text{ K}}$$

$$\boxed{Pf = 11.93\%}$$

**c)** at -20 °C;

$$Pf = \frac{1}{e}$$

$$Pf = \frac{T_h}{T_h - T_c}$$

$$Pf = \frac{298.15 \text{ K}}{(298.15 - 253.15) \text{ K}}$$

$$Pf = 6.63\%$$

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**3.59.** A typical automobile engine works with a cylinder temperature of 2000 °C and an exit temperature of 800 °C. A typical octane fuel (molar mass = 114.2 g mol<sup>-1</sup>) has an enthalpy of combustion of -5500 kJ mol<sup>-1</sup> and 1 dm<sup>3</sup> (0.264 U.S. gal) has a mass of 0.80 kg. Calculate the maximum amount of work that could be performed by the combustion of 10 dm<sup>3</sup> of the fuel.

**Solution:**

Given:  $T_{\text{cyl}} = 2000\text{ °C}$ ,  $T_{\text{exit}} = 800\text{ °C}$ ,  $M_{\text{fuel}} = 114.2\text{ g mol}^{-1}$ ,  $\Delta_c H = -5500\text{ kJ mol}^{-1}$

$$V = 1\text{ dm}^3, m = 0.80\text{ kg}$$

Required:  $w_{\text{max}}$  such that  $V = 10\text{ dm}^3$

We can first determine the efficiency of this automobile engine due to the fact that we are given both the exit and cylinder temperatures. Eq. 3.21 gives the efficiency for this system.

$$e = \frac{T_h - T_c}{T_h}$$

$$e = \frac{T_{\text{cyl}} - T_{\text{exit}}}{T_{\text{cyl}}}$$

$$e = \frac{(2273.15 - 1073.15)\text{ K}}{2273.15\text{ K}}$$

$$e = 0.528$$

Given the fuel's mass and molar mass, we can determine the number of moles involved in the reaction. We are initially told that 1 dm<sup>3</sup> (0.264 U.S. gal) has a mass of 0.80 kg. Since 1 dm<sup>3</sup> can be described as

1 dm<sup>3</sup> = 1 dm × 1 dm × 1 dm = 10 cm × 10 cm × 10 cm = 1000 mL = 1 L it follows that 1 liter of fuel is equivalent to 0.80 kg.

$$n = \frac{m}{M} \text{ for 1 liter}$$

$$n = \frac{800\text{ g}}{114.2\text{ g mol}^{-1}}$$

$$n = 7.005\text{ mol}$$

Using the enthalpy of combustion for the reaction, it is possible to determine the amount of energy produced (ie. the heat).

$$q = -n\Delta_c H^\circ$$

$$q = -(7.005\,254\,\text{mol})(-5500\,\text{kJ mol}^{-1})$$

$$q = 38\,528.8967\,\text{kJ} \rightarrow q = 3.85 \times 10^4\,\text{kJ}$$

Eq. 3.20 gives a modified version of the efficiency which can be used in conjunction with the value calculated in the first part of the problem in order to determine the work done during the combustion of the fuel.

$$e = \frac{w}{q_h}$$

$$w = eq_h$$

$$w = (0.528)(38\,528.8967\,\text{kJ})$$

$$w = 20\,343.257\,\text{kJ}$$

$$\boxed{w = 2.03 \times 10^4\,\text{kJ}}$$

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- 3.60.** The temperature of a building is maintained at 20 °C by means of a heat pump, and on a particular day the external temperature is 10 °C. The work is supplied to the heat pump by a heat engine that burns fuel at 1000 °C and operates at 20 °C. Calculate the performance factor for the system (i.e., the ratio of the heat delivered to the building to the heat produced by the fuel in the heat engine). Assume perfect efficiencies of the pump and the engine.

**Solution:**

Given:  $T_{\text{building}} = 20^\circ\text{C}$ ,  $T_{\text{ext}} = 10^\circ\text{C}$ ,  $T_{\text{burn}} = 1000^\circ\text{C}$ ,  $T_{\text{operate}} = 20^\circ\text{C}$

Required: performance factor

The efficiency of the reversible Carnot engine can be defined as the work done by the system during the cycle divided by the work that would have been done if all the heat absorbed at the higher temperature had been converted to work. From this statement, we can extract Eq. 3.20. We say that efficiency is unity (100% efficiency) only if the lower temperature is zero. Here, we are assuming that the efficiencies of the pump and the engine are perfect. This yields the following expression.

Eq. 3.22:

$$\frac{T_h - T_c}{T_h} = \frac{q_h + q_c}{q_h} \quad \text{or} \quad -\frac{T_h}{T_c} = \frac{q_h}{q_c}$$

Let the heat being supplied to the building be  $q_h$  at 20 °C. At the same time,  $q_c$  will be the heat taken in by the heat pump at 10 °C. With this information, it is possible to determine the amount of work supplied to the heat pump.

$$\begin{aligned} \frac{q_h}{q_c} &= -\frac{T_h}{T_c} \\ \frac{q_h}{q_c} &= -\frac{293.15 \text{ K}}{(-283.15 \text{ K})} \\ \frac{q_h}{q_c} &= \frac{293.15 \text{ K}}{283.15 \text{ K}} \\ \frac{q_h}{q_c} &= 1.035 \text{ 317} \end{aligned}$$

From Eq. 3.20 and Eq. 3.21 we get,

$$e = \frac{w}{q_h} = \frac{T_h - T_c}{T_h} = \frac{q_h - q_c}{q_h}$$

$$\text{since } -\frac{T_h}{T_c} = \frac{q_h}{q_c}$$

$$w = q_h - q_c$$

$$w = q_h \left( 1 - \frac{q_c}{q_h} \right)$$

$$w = 0.034\,112\,q_h$$

We must now consider the heat that is produced as a result of fuel combustion. Let  $q_h'$  be the heat produced by the fuel at  $1000^\circ\text{C}$ . On the other hand,  $q_c'$  will be equivalent to the heat being rejected at  $20^\circ\text{C}$ .

$$\frac{q_h'}{q_c'} = -\frac{T_h'}{T_c'}$$

$$\frac{q_h'}{q_c'} = -\frac{1273.15\,\text{K}}{(-293.15\,\text{K})}$$

$$\frac{q_h'}{q_c'} = \frac{1273.15\,\text{K}}{293.15\,\text{K}}$$

$$\frac{q_h'}{q_c'} = 4.342\,998$$

From Eq. 3.20 and Eq. 3.21 we get,

$$e = \frac{w}{q_h'} = \frac{T_h - T_c}{T_h} = \frac{q_h' - q_c'}{q_h'}$$

$$\text{since } -\frac{T_h'}{T_c'} = \frac{q_h'}{q_c'}$$

$$w = q_h' - q_c'$$

$$w = q_h' \left( 1 - \frac{q_c'}{q_h'} \right)$$

$$w = 0.769\,744\, q_h'$$

Setting both values for work equal to one another, it will be possible to solve for the performance factor.

$$w = 0.034\,112\, q_h = 0.769\,744\, q_h'$$

$$Pf = \frac{1}{e} = \frac{T_h}{T_h - T_c} = \frac{q_h}{q_h + q_c} = \frac{q_h}{q_h'}$$

$$Pf = \frac{0.769\,744}{0.034\,112}$$

$$\boxed{Pf = 22.57\%}$$

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**3.61.** Suppose that a refrigerator cools to 0 °C, discharges heat at 25 °C, and operates with 40% efficiency.

**a.** How much work would be required to freeze 1 kg of water ( $\Delta_f H = -6.02 \text{ kJ mol}^{-1}$ )?

**b.** How much heat would be discharged during the process?

**Solution:**

Given:  $T_{\text{cools}} = 0 \text{ }^{\circ}\text{C}$ ,  $T_{\text{discharges}} = 25 \text{ }^{\circ}\text{C}$ ,  $e = 40\%$

Required:  $w_{\text{freeze}}$ ,  $q_{\text{discharge}}$

First we should determine the amount of heat that must be removed from 1 kg of water in order to freeze it. This can be done using the number of moles in 1 kg (water) and the enthalpy of formation given above.

**a)** This yields,

$$q_c = n\Delta_f H^{\circ}$$

$$n = \frac{m}{M} = \frac{1000 \cancel{\text{g}}}{18.0152 \cancel{\text{g}} \text{ mol}^{-1}}$$

$$n = 55.508 \text{ 682 mol}$$

$$q_c = (55.508 \text{ 682 } \cancel{\text{mol}})(6.02 \text{ kJ } \cancel{\text{mol}^{-1}})$$

$$q_c = 334.16 \text{ kJ}$$

$$q_{\text{freeze}} = 3.34 \times 10^2 \text{ kJ}$$

The value for heat that we just calculated will be the amount of heat gained by the refrigerator during the cooling process. Assuming that we were able to work under 100% efficiency, we would have the following from Eq. 3.22;



$$\frac{T_h - T_c}{T_h} = \frac{q_h + q_c}{q_h} \text{ or } -\frac{T_h}{T_c} = \frac{q_h}{q_c}$$

$$-\frac{q_h}{q_c} = \frac{T_h}{T_c}$$

$$-\frac{q_h}{q_c} = \frac{298.15 \text{ K}}{273.15 \text{ K}}$$

$$-q_h = q_c \left( \frac{298.15 \text{ K}}{273.15 \text{ K}} \right) = 334.16 \text{ kJ} \times 1.091525$$

$$-q_h = 364.74 \text{ kJ}$$

The amount of heat discharged at 25 °C is therefore expressed as,

$$\boxed{-q_h = 365 \text{ kJ}} \rightarrow q_{\text{discharged}} = 365 \text{ kJ}$$

The work required to be supplied to the refrigerator can then be found by subtracting the amount of heat that must be removed from 1 kg of water in order to freeze it from the amount of heat discharged. We obtain,

$$w_{\text{supplied}} = |q_{\text{discharge}} - q_{\text{freeze}}|$$

$$w_{\text{supplied}} = |364.74 - 334.16| \text{ kJ}$$

$$w_{\text{supplied}} = 30.58 \text{ kJ}$$

We will now work under the given conditions (ie. efficiency is equal to 40%) in order to determine the amount of work required to freeze 1 kg of water. By inspection:

$$w_{\text{freeze}} = \frac{w_{\text{supplied}}}{e}$$

$$e = 0.40 = \frac{40}{100}$$

$$w_{\text{freeze}} = (30.58 \text{ kJ}) \times \frac{100}{40}$$

$$\boxed{w_{\text{freeze}} = 76.45 \text{ kJ}}$$

b) The amount of heat discharged at 25 °C at 40 percent efficiency is therefore given by the expression which defines the change in internal energy of a system:

$$\Delta U = q + w$$

$$\Delta U = q_{\text{freeze}} + w_{\text{freeze}}$$

$$\Delta U = 334.15 \text{ kJ} + 76.45 \text{ kJ}$$

$$\Delta U = q_{\text{discharged}}$$

$$q_{\text{discharged}}(25^\circ\text{C}) = 411 \text{ kJ}$$

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**3.62.** Show that (a)  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - \kappa P}{\kappa}$ , and (b)  $\left(\frac{\partial U}{\partial P}\right)_T = V(\kappa P - \alpha T)$ , where  $\kappa = \frac{-1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ , is called the isothermal compressibility coefficient.

$$\left[ \text{Use the relationship } \left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \right]$$

**Solution:**

On the basis of principles that have been developed and explored in the previous problems (Chapter 3), it is possible to derive a number of relationships between different thermodynamic quantities. We can derive equations that give the internal energy and the enthalpy in terms of pressure, volume and temperature.

**a)** Using the relationship ship given above and knowing that  $\kappa = \frac{-1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ ,  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - \kappa P}{\kappa}$

we have;

$$\left(\frac{\partial P}{\partial T}\right)_T = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = -\frac{\alpha}{\kappa}$$

Which can then be substituted into Eq. 3.128 in order to get,

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= -P + T \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial U}{\partial V}\right)_T &= -P + T \left(\frac{\alpha}{\kappa}\right) \end{aligned}$$

expanding to obtain,

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - \kappa P}{\kappa}}$$

**b)** Using the chain rule for partial differentiation given in Appendix C we can then say that:

if we have  $\left(\frac{\partial z}{\partial x}\right)_y$  then,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Then according to Euler's Reciprocity Theorem, we will get the following:

$$\left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y = \left[ \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right]_x$$

$$\left( \frac{\partial z}{\partial x} \right)_y = \frac{1}{\left( \frac{\partial x}{\partial z} \right)_y}$$

$$0 = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z$$

$$\left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1$$

$$\left( \frac{\partial z}{\partial x} \right)_y = - \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z$$

We can now use what we have been given above in order to prove the given relationship.

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

therefore,

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

since;

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - \kappa P}{\kappa} \text{ and } \left(\frac{\partial V}{\partial P}\right)_T = -\kappa V$$

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\alpha T - \kappa P}{\cancel{\kappa}}\right)(-\cancel{\kappa}V)$$

simplify to get,

$$\boxed{\left(\frac{\partial U}{\partial P}\right)_T = V(\kappa P - \alpha T)}$$

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**3.63.** Derive an equation of state from

$$dH = T dS + V dP$$

by taking the partial derivative with respect to  $P$  at constant temperature. Then use the appropriate Maxwell relation and the definition of  $\alpha$  to express the partial in terms of easily measured quantities.

**Solution:**

Recall that for Maxwell Relations, they are used to describe an infinitesimal process involving only  $PV$  work. This means that we are able to combine the First and Second Laws of Thermodynamics. This is shown by Eq. 3.105:

$$dU = dw + dq = -PdV + TdS$$

Since we are already given the expression above for enthalpy let us find the partial derivative.

$$dH = T dS + V dP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \cancel{\left(\frac{\partial P}{\partial P}\right)_T}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V$$

$$\text{Knowing that } -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P,$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

From Eq. 3.139 we are given the following:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \text{ which then rearranges to } \left(\frac{\partial V}{\partial T}\right)_P = \alpha V \text{ and making the last substitution we obtain,}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T(\alpha V)$$

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = V(1 - \alpha T)}$$

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**3.64.** Derive expressions for (a)  $\alpha$  and (b)  $\kappa$  for an ideal gas.

**Solution:**

We have seen many times by now that the Ideal Gas Law is given by,  $PV=nRT$ . Remember from the previous problem that we are given the value of  $\alpha$  in Eq. 3.139 which states that:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

We can also determine the relationship for  $\kappa$  by Eq. 3.142 which gives:

$$\kappa = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

**a)** Since the volume is the important variable in this case, let us rearrange the Ideal Gas Law to isolate for it.

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V_m = \frac{RT}{P} \text{ therefore,}$$

$$\left( \frac{\partial V_m}{\partial T} \right)_P = \frac{R}{P}$$

Let us make the appropriate substitution into the equation for the cubic expansion coefficient to get,



$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$\alpha = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_P$$

$$\left( \frac{\partial V_m}{\partial T} \right)_P = \frac{R}{P}$$

$$\alpha = \frac{1}{V_m} \left( \frac{R}{P} \right)$$

$$\alpha = \frac{R}{V_m P}$$

$$\boxed{\alpha = \frac{1}{T}}$$

**b)** For the second part of this problem, we will use the same rearrangement of the Ideal Gas Law, however, we will take the partial derivative with respect to the pressure while keeping the temperature constant. This will yield the following:

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V_m = \frac{RT}{P}$$

$$\left( \frac{\partial V_m}{\partial P} \right)_T = -\frac{RT}{P^2}$$

$$\kappa = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial P} \right)_T$$

$$\kappa = \frac{1}{V_m} \left( -\frac{RT}{P^2} \right)$$

$$\kappa = \frac{1}{\left( \frac{RT}{P} \right)} \left( -\frac{RT}{P^2} \right) \rightarrow \left( \frac{\cancel{P}}{\cancel{RT}} \right) \left( -\frac{\cancel{RT}}{P^2} \right)$$

$$\boxed{\kappa = -\frac{1}{P}}$$

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**\*3.65.** Suppose that a gas obeys the van der Waals equation

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Prove that:

$$\left(\frac{\partial U}{\partial V_m}\right)_T = \frac{a}{V_m^2}$$

**Solution:**

Remember that Eq. 3.105 represents a process which is infinitesimal and involves only  $PV$  work. We have combined both the First and Second Laws of Thermodynamics.

$$dU = dw + dq = -PdV + TdS$$

We will continue by using the second part of this expression as it relates back to the Van der Waals equation. Let us take the partial derivative with respect to the volume while keeping the temperature constant.

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V_m}\right)_T = T\left(\frac{\partial S}{\partial V_m}\right)_T - P\left(\frac{\partial V_m}{\partial V_m}\right)_T$$

$$\left(\frac{\partial U}{\partial V_m}\right)_T = T\left(\frac{\partial S}{\partial V_m}\right)_T - P$$

Now since we know that  $-PdV + TdS$  and  $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V_m}\right)_T$  then we can make this substitution into the above (this is given by Eq. 3.124):

$$\left(\frac{\partial U}{\partial V_m}\right)_T = T\left(\frac{\partial S}{\partial V_m}\right)_T - P$$

$$\left(\frac{\partial U}{\partial V_m}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

From the Van der Waals equation given in the problem,

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{(V_m - b)} = \frac{1}{T} \left(P + \frac{a}{V_m^2}\right)$$

We can now substitute this into the above and simplify which will yield:

$$\left(\frac{\partial U}{\partial V_m}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{(V_m - b)} = \frac{1}{T} \left(P + \frac{a}{V_m^2}\right)$$

$$\left(\frac{\partial U}{\partial V_m}\right)_T = \cancel{T} \left[ \frac{1}{\cancel{T}} \left(P + \frac{a}{V_m^2}\right) \right] - P$$

$$\left(\frac{\partial U}{\partial V_m}\right)_T = \left(\cancel{T} + \frac{a}{V_m^2}\right) - \cancel{T}$$

$$\boxed{\left(\frac{\partial U}{\partial V_m}\right)_T = \frac{a}{V_m^2}}$$

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**\*3.66.** Obtain an expression for the Joule-Thomson coefficient for a gas obeying the equation of state:

$$P(V_m - b) = RT$$

in terms of  $R$ ,  $T$ ,  $P$ ,  $V_m$ , and  $C_{P,m}$ .

**Solution:**

From Chapter 2 we have seen that the Joule-Thomson coefficient is given by Eq. 2.108:

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H \approx \frac{\Delta T}{\Delta P}$$

We must also realize that the enthalpy is given by  $dH = TdS + VdP$  so we need to take the partial derivative of  $dH$  both with respect to  $T$  and  $P$  in order to solve for the final expression. Recall that from Eq. 2.109 and Eq. 2.110:

$$dH = \left( \frac{\partial H}{\partial P} \right)_T dP + \left( \frac{\partial H}{\partial T} \right)_P dT = 0$$

$$\left( \frac{\partial H}{\partial P} \right)_T = - \left( \frac{\partial H}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_T = -C_{P,\mu}$$

Using Euler's Chain Rule, we can redefine the expression given above for the Joule-Thomson coefficient.

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H \approx \frac{\Delta T}{\Delta P}$$

$$\left( \frac{\partial T}{\partial P} \right)_H = - \frac{\left( \frac{\partial H}{\partial P} \right)_T}{\left( \frac{\partial H}{\partial T} \right)_P} = - \left( \frac{\partial \mathcal{H}}{\partial P} \right)_{\mathcal{T}} \left( \frac{\partial \mathcal{T}}{\partial \mathcal{H}} \right)_{\mathcal{P}}$$

$$\left( \frac{\partial T}{\partial P} \right)_H = - \frac{1}{C_{P,\mu}} \left( \frac{\partial H}{\partial P} \right)_T$$

Let us now define  $\left( \frac{\partial H}{\partial P} \right)_T$  using the relationship between  $T$ ,  $P$  and  $V$  and enthalpy.

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\cancel{\left(\frac{\partial P}{\partial P}\right)_T}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Since we know that according to Eq. 3.125:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

We can make this substitution into the above equation to get,

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Let us now substitute this expression into that of the Joule-Thomson coefficient to obtain,

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H \approx \frac{\Delta T}{\Delta P}$$

$$\mu = -\frac{1}{C_p} \left( \frac{\partial H}{\partial P} \right)_T$$

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$$

$$\mu = -\frac{1}{C_p} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right]$$

$$\mu = \frac{T \left( \frac{\partial V}{\partial T} \right)_P - V}{C_p}$$

For a single mole of this gas (as was given by the equation of state) we can then write,

$$\mu = \frac{T \left( \frac{\partial V}{\partial T} \right)_P - V}{C_p}$$

$$\mu = \frac{T \left( \frac{\partial V_m}{\partial T} \right)_P - V_m}{C_{p,m}}$$

$$P(V_m - b) = RT$$

$$\left(\frac{\partial V_m}{\partial T}\right)_P = \frac{R}{P}$$
$$\mu = \frac{T\left(\frac{\partial V_m}{\partial T}\right)_P - V_m}{C_{P,m}}$$
$$\mu = \frac{T\left(\frac{R}{P}\right) - V_m}{C_{P,m}}$$
$$\boxed{\mu = \frac{\frac{RT}{P} - V_m}{C_{P,m}}}$$

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**\*3.67.** Derive the following equations:

$$\text{a. } C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P$$

$$\text{b. } \left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P$$

**Solution:**

**a)** Using Eq. 3.119 we can see that,

$$\left( \frac{\partial G}{\partial P} \right)_T = V \text{ and } \left( \frac{\partial G}{\partial T} \right)_P = -S$$

We will use the second expression and differentiate each side (with respect to  $T$  while keeping  $P$  constant) in order to obtain the desired equation.

$$\left( \frac{\partial G}{\partial T} \right)_P = -S$$

$$\left( \frac{\partial^2 G}{\partial T^2} \right)_P = - \left( \frac{\partial S}{\partial T} \right)_P$$

Eq. 3.55 gives us  $dS = \frac{q_{rev}}{T}$  and we can also say that  $dS = \frac{C_p dT}{T}$  at constant pressure. Therefore, we can make this substitution into the above expression to obtain,

$$\left( \frac{\partial^2 G}{\partial T^2} \right)_P = - \left( \frac{\partial S}{\partial T} \right)_P$$

$$\left( \frac{\partial^2 G}{\partial T^2} \right)_P = - \frac{C_p}{T}$$

$$\boxed{C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P}$$

b)  $C_P$  is defined by Eq. 2.27 which states that:

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

Using the Euler Reciprocity Theorem we can write,

$$\left( \frac{\partial C_P}{\partial P} \right)_T = \left[ \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial T} \right)_P \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial P} \right)_T \right]_P$$

From problem 3.66 we have the following:

$$dH = VdP + TdS$$

$$\left( \frac{\partial H}{\partial P} \right)_T = V \left( \frac{\partial P}{\partial P} \right)_T + T \left( \frac{\partial S}{\partial P} \right)_T$$

$$\left( \frac{\partial H}{\partial P} \right)_T = V + T \left( \frac{\partial S}{\partial P} \right)_T$$

$$\text{since } VdP = -TdS$$

$$-\left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\partial S}{\partial P} \right)_T$$

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$$

This can now be substituted into the expression derived from Eq. 2.27.

$$\begin{aligned}
 \left( \frac{\partial C_p}{\partial P} \right)_T &= \left[ \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial T} \right)_P \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial P} \right)_T \right]_P \\
 \left[ \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial P} \right)_T \right]_P &= \frac{\partial}{\partial T} \left( V - T \left( \frac{\partial V}{\partial T} \right)_P \right) \\
 \left[ \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial P} \right)_T \right]_P &= \cancel{\left( \frac{\partial V}{\partial T} \right)_P} - T \left( \frac{\partial^2 V}{\partial T^2} \right)_P - \cancel{\left( \frac{\partial V}{\partial T} \right)_P} \\
 \boxed{\left( \frac{\partial C_p}{\partial P} \right)_T} &= -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P
 \end{aligned}$$

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**\*3.68.** Starting with the definition of the Helmholtz energy,  $A = U - TS$ , prove that the change in Helmholtz energy for a process at constant temperature is the total work ( $PV$  and non- $PV$ ). (This relationship holds without any restriction as to volume or pressure changes.)

**Solution:**

We have already been given the equation that defines the Helmholtz energy. Now let us define it for an infinitesimal process.

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

At constant temperature then the above becomes:

$$dA = dU - TdS - SdT$$

since  $dU = dw + dq$  then;

$$dA = dw + dq - TdS - SdT$$

However, knowing that  $dq = TdS$  so we can say that:

$$dA = dU - TdS - SdT$$

$$dU = dw + dq$$

$$dA = dw + \cancel{dq} - \cancel{TdS} - SdT$$

$$\boxed{dA = dw - SdT}$$

Using the First Law of Thermodynamics which states that:  $dU = TdS - PdV$  we can change the work so that it only considers pressure-volume work in order to obtain,

$$dA = dU - TdS - SdT$$

$$dU = TdS - PdV$$

$$dA = \cancel{TdS} - PdV - \cancel{TdS} - SdT$$

$$\boxed{dA = -PdV - SdT}$$

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**\*3.69.** Prove that if a gas obeys Boyle's law and if in addition  $(\partial U/\partial V)_T = 0$ , it must obey the equation of state  $PV = \text{constant} \times T$ .

**Solution:**

From the previous problem and the First Law of Thermodynamics, recall that (Eq. 3.105):

$$dU = dw + dq = TdS - PdV$$

Let us take the partial differential with respect to volume while keeping temperature constant.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = 0$$

We can make the following substitution into the above equation to obtain,

$$TdS = PdV$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = 0$$

This means that  $\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}$  and this can be integrated to get,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}$$

$$\int \frac{P}{T} = \ln\left(\frac{P}{T}\right)$$

And using the rules for logarithms,

$$\ln\left(\frac{P}{T}\right) = \ln(P) - \ln(T) = 0$$

$$\ln(P) = \ln(T) + C$$

Thus,  $PV = C \times T$  when taking the exponential for the expression.

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**\*3.70.** Derive the relationship

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

and confirm that it applies to an ideal gas.

**Solution:**

We will again use Euler's Chain Rule and Reciprocity Theorem for this problem. This will give us the following,

$$\left(\frac{\partial S}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_S}{\left(\frac{\partial U}{\partial S}\right)_V} \rightarrow -\left(\frac{\cancel{\partial U}}{\partial V}\right)_S \left(\frac{\partial S}{\cancel{\partial U}}\right)_V$$

Using the Maxwell Relation given by Eq. 3.116, we observe,

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \text{ and } \left(\frac{\partial U}{\partial S}\right)_V = T$$

Which proves that:

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_U &= -\frac{\left(\frac{\partial U}{\partial V}\right)_S}{\left(\frac{\partial U}{\partial S}\right)_V} \\ \left(\frac{\partial S}{\partial V}\right)_U &= -\left(\frac{-P}{T}\right) \\ \left(\frac{\partial S}{\partial V}\right)_U &= \left(\frac{P}{T}\right) \end{aligned}$$

For an Ideal Gas, we should note that the internal energy only depends on the temperature. This will allow us to write,

$$\left(\frac{\partial S}{\partial V}\right)_U = \left(\frac{\partial S}{\partial V}\right)_T$$

For an Isothermal Process involving  $n$  moles of Ideal Gas,

$$dS = nR d \ln V$$

$$dS = \frac{nR dV}{V}$$

$$\text{and since } PV = nRT \rightarrow \frac{P}{T} = \frac{nR}{V}$$

$$dS = \frac{PdV}{T}$$

Thus,

$$dS = \frac{PdV}{T}$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \frac{P}{T} \text{ and therefore } \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}}$$

[Back to Problem 3.70](#)

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**3.71.** Starting from Eq. 3.160,

**a.** Show that  $\ln \left( \frac{f_2}{f_1} \right) = \int_{P_1}^{P_2} \left( \frac{Z-1}{P} \right) dP$ , where  $Z = \frac{PV_m}{RT}$ .

**b.** For a nonideal gas, the equation of state is given as  $PV_m = RT + (b - A/RT^{2/3})P$  (see Example 1.6, p. 42). Derive an expression to find the fugacity of the gas at a given temperature and pressure when the constants  $b$  and  $A$  are given.

**Solution:**

**a)** If  $P_1$  is a sufficiently low pressure, Eq. 3.160 states that:

$$RT \ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} \left( V_m - \frac{RT}{P} \right) dP$$

This relationship describes the fugacity for a gas. Let us divide both sides by  $RT$  and using the definition of the compression factor (given in Chapter 1, Eq. 1.98)  $Z$ , we will obtain the following:

$$RT \ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} \left( \frac{PV_m - RT}{P} \right) dP$$

$$Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$$

$$\ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} \left( \frac{\frac{PV_m - RT}{RT}}{P} \right) dP$$

$$\ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} \left( \frac{\frac{PV_m}{RT} - 1}{P} \right) dP$$

$$\boxed{\ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} \left( \frac{Z-1}{P} \right) dP}$$

b) Let's first substitute the equation of state into the expression for the compression factor.

$$Z = \frac{PV_m}{RT}$$

$$PV_m = RT + \left(b - A / RT^{2/3}\right)P$$

$$Z = \frac{\left[RT + \left(b - A / RT^{2/3}\right)P\right]}{RT}$$

$$Z = 1 + \left(b - A / RT^{2/3}\right)\left(\frac{P}{RT}\right)$$

$$Z = 1 + \left[\frac{b}{(RT)} - \frac{A}{(RT^{5/3})}\right]P$$

$$\frac{Z-1}{P} = \frac{b}{(RT)} - \frac{A}{(RT^{5/3})}$$

Now we can set  $P_I=0$  and integrate the expression to obtain,

$$\ln \frac{f}{P_2} = \int_0^{P_2} \left( \frac{Z-1}{P} \right) dP$$

$$\ln \frac{f}{P_2} = \left( \frac{b}{RT} - \frac{A}{RT^{5/3}} \right) \Big|_0^{P_2}$$

$$\ln \frac{f}{P_2} = \left( \frac{b}{RT} - \frac{A}{RT^{5/3}} \right) (P_2 - 0)$$

$$\boxed{\ln \frac{f}{P_2} = \left( \frac{b}{RT} - \frac{A}{RT^{5/3}} \right) P_2}$$

[Back to Problem 3.71](#)

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**3.72.** The van der Waals constants for methane in older units are  $a = 2.283 \text{ L}^2 \text{ bar mol}^{-2}$  and  $b = 0.0428 \text{ L mol}^{-1}$ . Expressing the compression factor as (see Problem 1.52 in Chapter 1):

$$Z = 1 + \frac{1}{RT} \left( b - \frac{a}{RT} \right) P + \left( \frac{b}{RT} \right)^2 P^2,$$

Find the fugacity of methane at 500 bar and 298 K.

**Solution:**

We are able to use the same expression (for fugacity) we have just derived in the previous problem. This yields the following:

$$\ln \left( \frac{f}{P} \right) = \int_0^P \left( \frac{Z-1}{P} \right) dP$$

$$Z = 1 + \left( \frac{b}{RT} - \frac{a}{RT^2} \right) P$$

$$\frac{Z-1}{P} = \frac{b}{RT} - \frac{a}{RT^2}$$

$$\frac{Z-1}{P} = \frac{1}{RT} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{RT} \right)^2 P$$

$$\ln \left( \frac{f}{P} \right) = \int_0^P \left[ \frac{1}{RT} \left( b - \frac{a}{RT} \right) + \left( \frac{b}{RT} \right)^2 P \right] dP$$

$$\ln \left( \frac{f}{P} \right) = \int_0^P \left[ \frac{1}{RT} \left( b - \frac{a}{RT} \right) \right] dP + \left( \frac{b}{RT} \right)^2 \int_0^P P dP$$

$$\ln \left( \frac{f}{P} \right) = \frac{1}{RT} \left( b - \frac{a}{RT} \right) P + \frac{1}{2} \left( \frac{b}{RT} \right)^2 P^2 = -0.622 \ 84$$

The fugacity of the gas can then be found.

$$\ln\left(\frac{f}{P}\right) = -0.622\,84$$

$$\cancel{\ln}\left(\frac{f}{P}\right) = e^{(-0.622\,84)}$$

$$f = Pe^{(-0.622\,84)}$$

$$f = (500)e^{(-0.622\,84)}$$

$$\boxed{f = 268\text{ bar}}$$

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# CHAPTER 4

## Chemical Equilibrium

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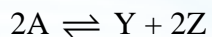
# Problems and Solutions

**Chapter 4**

*\*problems with an asterisk are slightly more demanding*

**Equilibrium Constants**

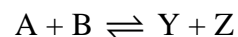
**4.1.** A reaction occurs according to the equation:



If in a volume of  $5 \text{ dm}^3$  we start with 4 mol of pure A and find that 1 mol of A remains at equilibrium, what is the equilibrium constant  $K_c$ ?

[Solution](#)

**4.2.** The equilibrium constant for a reaction below is 0.1:



What amount of A must be mixed with 3 mol of B to yield, at equilibrium, 2 mol of Y?

[Solution](#)

**4.3.** The equilibrium constant for the reaction below is  $0.25 \text{ dm}^6 \text{ mol}^{-2}$



In a volume of  $5 \text{ dm}^3$ , what amount of A must be mixed with 4 mol of B to yield 1 mol of Z at equilibrium?

[Solution](#)

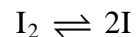
**4.4.** The equilibrium constant  $K_c$  for the reaction:



is  $0.0271 \text{ mol dm}^{-3}$  at 1100 K. Calculate  $K_p$  at that temperature.

[Solution](#)

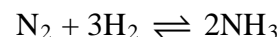
- 4.5. When gaseous iodine is heated, dissociation occurs:



It was found that when 0.0061 mol of iodine was placed in a volume of 0.5 dm<sup>3</sup> at 900 K, the degree of dissociation (the fraction of the iodine that is dissociated) was 0.0274. Calculate  $K_c$  and  $K_P$  at that temperature.

[Solution](#)

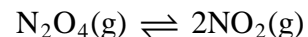
- 4.6. It has been observed with the ammonia equilibrium:



that under certain conditions the addition of nitrogen to an equilibrium mixture, *with the temperature and pressure held constant*, causes further dissociation of ammonia. Explain how this is possible. Under what particular conditions would you expect this to occur? Would it be possible for added hydrogen to produce the same effect?

[Solution](#)

- 4.7. Nitrogen dioxide, NO<sub>2</sub>, exists in equilibrium with dinitrogen tetroxide, N<sub>2</sub>O<sub>4</sub>:

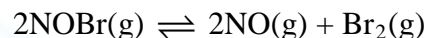


At 25.0 °C and a pressure of 0.597 bar the density of the gas is 1.477 g dm<sup>-3</sup>. Calculate the degree of dissociation under those conditions, and the equilibrium constants  $K_c$ ,  $K_P$ , and  $K_x$ . What shift in equilibrium would occur if the pressure were increased by the addition of helium gas?

[Solution](#)



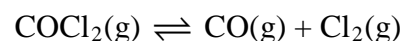
- 4.8. At 25.0 °C the equilibrium:



is rapidly established. When 1.10 g of NOBr is present in a 1.0-dm<sup>3</sup> vessel at 25.0 °C the pressure is 0.355 bar. Calculate the equilibrium constants  $K_P$ ,  $K_c$ , and  $K_x$ .

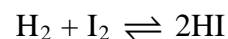
[Solution](#)

- 4.9. At 100 °C and 2 bar pressure the degree of dissociation of phosgene is  $6.30 \times 10^{-5}$ . Calculate  $K_P$ ,  $K_c$ , and  $K_x$  for the dissociation:



[Solution](#)

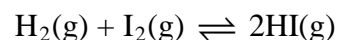
- 4.10. In a study of the equilibrium



1 mol of H<sub>2</sub> and 3 mol of I<sub>2</sub> gave rise at equilibrium to  $x$  mol of HI. Addition of a further 2 mol of H<sub>2</sub> gave an additional  $x$  mol of HI. What is  $x$ ? What is  $K$  at the temperature of the experiment?

[Solution](#)

- \*4.11. The equilibrium constant for the reaction below is 20.0 at 40.0 °C:



The vapor pressure of solid iodine is 0.10 bar at that temperature. If 12.7 g of solid iodine are placed in a 10-dm<sup>3</sup> vessel at 40.0 °C, what is the minimum amount of hydrogen gas that must be introduced in order to remove all the solid iodine?

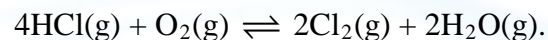
[Solution](#)

- 4.12.** The degree of dissociation  $\alpha$  of  $\text{N}_2\text{O}_4(\text{g})$  is 0.483 at 0.597 bar and 0.174 at 6.18 bar. The temperature is 298 K for both measurements. Calculate  $K_P$ ,  $K_c$ , and  $K_x$  in each case.

(Hint: See Example 4.1.)

[Solution](#)

- 4.13.** One mole of HCl mixed with oxygen is brought into contact with a catalyst until the following equilibrium has been established:



If  $y$  mol of  $\text{HCl}$  is formed, derive an expression for  $K_P$  in terms of  $y$  and the partial pressure of oxygen.

(Hint: First develop expressions for the ratios  $x_{\text{Cl}_2}/x_{\text{HCl}}$  and  $x_{\text{H}_2\text{O}}/x_{\text{Cl}_2}$  in terms of  $y$  and  $P_{\text{O}_2}$ .)

[Solution](#)

- 4.14.** Using the result of Problem 4.13, evaluate  $K_P$  for an experiment in which 49%  $\text{HCl}$  and 51%  $\text{O}_2$  are brought into contact with a catalyst until the reaction is complete at 1 bar and 480 °C. The fraction of  $\text{HCl}$  converted per mole is found to be 0.76.

[Solution](#)

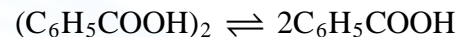
- 4.15.** 10.0 g of  $\text{HI}$  is introduced into an evacuated vessel at 731 K and allowed to reach equilibrium. Find the mole fractions of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  present at equilibrium.  $K_P = K_c = K_x = 65.0$  for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ .

(Hint: see Example 4.2)

[Solution](#)

**Equilibrium Constants and Gibbs Energy Changes**

**4.16.** The equilibrium constant for the reaction



in benzene solution at 10 °C is  $2.19 \times 10^{-3} \text{ mol dm}^{-3}$ .

**a.** Calculate  $\Delta G^\circ$  for the dissociation of the dimer.

**b.** If 0.1 mol of benzoic acid is present in 1 dm<sup>3</sup> of benzene at 10 °C, what are the concentrations of the monomer and of the dimer?

[Solution](#)

**4.17.** At 3000 K the equilibrium partial pressures of CO<sub>2</sub>,

CO, and O<sub>2</sub> are 0.6, 0.4, and 0.2 atm, respectively. Calculate  $\Delta G^\circ$  at 3000 K for the reaction:

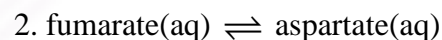


[Solution](#)

**4.18.** The conversion of malate into fumarate:



is endergonic at body temperature, 37 °C;  $\Delta G^\circ$  is 2.93 kJ mol<sup>-1</sup>. In metabolism the reaction is coupled with



for which  $\Delta G^\circ$  is – 15.5 kJ mol<sup>-1</sup> at 37 °C.

**a.** Calculate  $K_c$  for reaction 1.

**b.** Calculate  $K_c$  for reaction 2.

**c.** Calculate  $K_c$  and  $\Delta G^\circ$  for the coupled reaction 1 + 2.

[Solution](#)

**4.19.** From the data in Appendix D, deduce the  $\Delta G^\circ$  and  $K_P$  values for the following reactions at 25.0 °C:

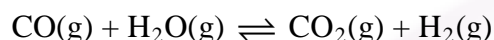
- a.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- b.  $2\text{H}_2(\text{g}) + \text{C}_2\text{H}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g})$
- c.  $\text{H}_2(\text{g}) + \text{C}_2\text{H}_4(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g})$
- d.  $2\text{CH}_4(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$

[Solution](#)

**4.20.** Calculate  $K_c$  and  $K_x$  for each of the reactions in Problem 4.19 assuming total pressures of 1 bar in each case.

[Solution](#)

**4.21.** At 25.0 °C the equilibrium constant for the reaction:

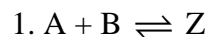


is  $1.00 \times 10^{-5}$ , and  $\Delta S^\circ$  is  $41.8 \text{ J K}^{-1} \text{ mol}^{-1}$ .

- a. Calculate  $\Delta G^\circ$  and  $\Delta H^\circ$  at 25.0 °C.
- b. Suppose that 2 mol of CO and 2 mol of  $\text{H}_2\text{O}$  are introduced into a  $10\text{-dm}^3$  vessel at 25.0 °C. What are the amounts of CO,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{H}_2$  at equilibrium?

[Solution](#)

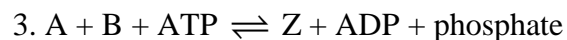
**4.22.** Suppose that there is a biological reaction:



for which the  $\Delta G^\circ$  value at 37.0 °C is  $23.8 \text{ kJ mol}^{-1}$ . (Standard state =  $1 \text{ mol dm}^{-3}$ .) Suppose that an enzyme couples this reaction with



for which  $\Delta G^\circ = -31.0 \text{ kJ mol}^{-1}$ . Calculate the equilibrium constant at 37.0 °C for these two reactions and for the coupled reaction



[Solution](#)

- 4.23. The equilibrium between citrate and isocitrate involves *cis*-aconitate as an intermediate:



At 25 °C and pH 7.4 it was found that the molar composition of the mixture was:

90.9%	Citrate
2.9%	<i>cis</i> -aconitate
6.2%	Isocitrate

Calculate the equilibrium constants for the individual reactions, and for the overall reaction, and  $\Delta G^\circ$  for the citrate-isocitrate system.

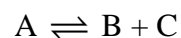
[Solution](#)

- 4.24. The solubility product of  $\text{Cr}(\text{OH})_3$  is  $3.0 \times 10^{-29} \text{ mol}^4 \text{ dm}^{-12}$  at 25 °C. What is the solubility of  $\text{Cr}(\text{OH})_3$  in water at this temperature?

[Solution](#)

### Temperature Dependence of Equilibrium Constants

- 4.25. A gas reaction:

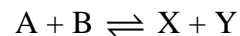


is endothermic and its equilibrium constant  $K_P$  is 1 bar at 25 °C.

- What is  $\Delta G^\circ$  at 25 °C (standard state: 1 bar)?
- Is  $\Delta S^\circ$ , with the same standard state, positive or negative?
- For the standard state of 1 *M*, what are  $K_c$  and  $\Delta G^\circ$ ?
- Will  $K_P$  at 40 °C be greater than or less than 1 bar?
- Will  $\Delta G^\circ$  at 40 °C (standard state: 1 bar) be positive or negative?

[Solution](#)

**4.26.** A solution reaction:

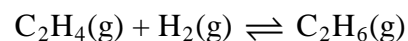


is endothermic, and  $K_c$  at 25 °C is 10.

- a. Is the formation of X + Y exergonic at 25 °C?
- b. Will raising the temperature increase the equilibrium yield of X + Y?
- c. Is  $\Delta S^\circ$  positive or negative?

[Solution](#)

**4.27.** From the data given in Appendix D, for the reaction:

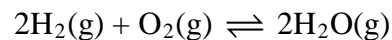


Calculate the following:

- a.  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 25 °C; what is the standard state?
- b.  $K_P$  at 25 °C.
- c.  $K_c$  at 25 °C (standard state: 1 M).
- d.  $\Delta G^\circ$  at 25 °C (standard state: 1 M).
- e.  $\Delta S^\circ$  at 25 °C (standard state: 1 M).
- f.  $K_P$  at 100 °C, on the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent.

[Solution](#)

**4.28.** From the data in Appendix D, for the reaction:

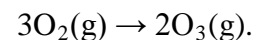


Calculate the following:

- a.  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 25 °C (standard state: 1 bar).
- b.  $K_P$  at 25 °C.
- c.  $\Delta G^\circ$  and  $K_P$  at 2000 °C, on the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent.

[Solution](#)

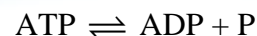
- 4.29.** Calculate the equilibrium constant at 400 K for the reaction:



where  $\Delta_f G^\circ(\text{O}_3, \text{g}) = 163.2 \text{ kJ mol}^{-1}$ .

[Solution](#)

- 4.30.** The hydrolysis of adenosine triphosphate to give adenosine diphosphate and phosphate can be represented by:



The following values have been obtained for the reaction at 37 °C (standard state: 1 M):

$$\Delta G^\circ = -31.0 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -20.1 \text{ kJ mol}^{-1}$$

- Calculate  $\Delta S^\circ$ .
- Calculate  $K_c$  at 37 °C.
- On the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, calculate  $\Delta G^\circ$  and  $K_c$  at 25 °C.

[Solution](#)

- 4.31.** Thermodynamic data for *n*-pentane(g) and neo-pentane(g) (standard state: 1 bar and 25 °C) are as follows:

Compound	Enthalpy of Formation, $\Delta H_f^\circ \text{ kJ mol}^{-1}$	Entropy, $S^\circ \text{ J K}^{-1} \text{ mol}^{-1}$
<i>n</i> -Pertane(g)	- 146.44	349.0
Neopentane(g)	- 165.98	306.4

- Calculate  $\Delta G^\circ$  for *n*-pentane  $\rightarrow$  neopentane.
- Pure *n*-pentane is in a vessel at 1 bar and 25 °C, and a catalyst is added to bring about the equilibrium between *n*-pentane and neopentane. Calculate the final partial pressures of the two isomers.

[Solution](#)



- 4.32.** a. An equilibrium constant  $K_c$  is increased by a factor of 3 when the temperature is raised from 25.0 °C to 40.0 °C. Calculate the standard enthalpy change.
- b. What is the standard enthalpy change if instead  $K_c$  is *decreased* by a factor of 3 under the same conditions?

[Solution](#)

- 4.33.** a. The ionic product  $[H^+][OH^-]$ , which is the equilibrium constant for the dissociation of water;



is  $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at 25.0 °C and  $1.45 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at 30.0 °C. Deduce  $\Delta H^\circ$  and  $\Delta S^\circ$  for the process.

- b. Calculate the value of the ionic product at body temperature (37 °C).

[Solution](#)

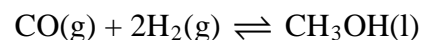
- 4.34.** The equilibrium constant  $K_P$  for the reaction  $I_2(g) + \text{cyclopentane}(g) \rightleftharpoons 2 HI(g) + \text{cyclopentadiene}(g)$  varies with temperatures according to the equation:

$$\log_{10}(K_P/\text{bar}) = 7.55 - 4844/(T/K)$$

- a. Calculate  $K_P$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  (standard state: 1 bar) at 400 °C.
- b. Calculate  $K_c$  and  $\Delta G^\circ$  (standard state: 1 M) at 400 °C.
- c. If  $I_2$  and cyclopentane are initially at 400 °C and at concentrations of 0.1 M, calculate the final equilibrium concentrations of  $I_2$ , cyclopentane, HI, and cyclopentadiene.

[Solution](#)

- 4.35.** From the data in Appendix D, for the synthesis of methanol,

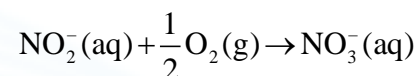


Calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  and the equilibrium constant at 25 °C.

[Solution](#)



- 4.36.** The bacterium *nitrobacter* plays an important role in the “nitrogen cycle” by oxidizing nitrite to nitrate. It obtains the energy it requires for growth from the reaction

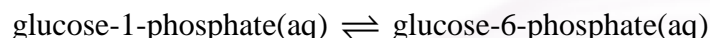


Calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  for this reaction from the following data, at 25 °C:

Ion	$\frac{\Delta_f H^\circ}{\text{kJ mol}^{-1}}$	$\frac{\Delta_f G^\circ}{\text{kJ mol}^{-1}}$
$\text{NO}_2^-$	-104.6	-37.2
$\text{NO}_3^-$	-207.4	-111.3

[Solution](#)

- 4.37.** When the reaction:

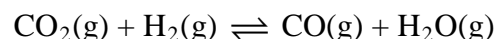


is at equilibrium at 25 °C, the amount of glucose-6-phosphate present is 95% of the total.

- Calculate  $\Delta G^\circ$  at 25 °C.
- Calculate  $\Delta G$  for reaction in the presence of  $10^{-2}$  M glucose-1-phosphate and  $10^{-4}$  M glucose-6-phosphate. In which direction does reaction occur under these conditions?

[Solution](#)

- 4.38.** From the data in Appendix D, for the reaction



Calculate the following:

- $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  (standard state: 1 bar and 25 °C).
- The equilibrium constant at 25 °C.
- From the heat capacity data in Table 2.1, obtain an expression for  $\Delta H^\circ$  as a function of temperature.
- Obtain an expression for  $\ln K_P$  as a function of temperature.
- Calculate  $K_P$  at 1000 K.

[Solution](#)

- 4.39.** Irving Langmuir [*J. Amer. Chem. Soc.*, 28, 1357 (1906)] studied the dissociation of  $\text{CO}_2$  into CO and  $\text{O}_2$  by bringing the gas at 1 atm pressure into contact with a heated platinum wire. He obtained the following results:

$T/\text{K}$	Percent Dissociation
1395	0.0140
1443	0.0250
1498	0.0471

Calculate  $K_P$  for  $2\text{CO}_2(\text{g}) = 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$  at each temperature, and estimate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  at 1395 K.

[Solution](#)

- 4.40.** G. Stark and M. Bodenstein [*Z. Electrochem.*, 16, 961(1910)] carried out experiments in which they sealed iodine in a glass bulb and measured the vapor pressure. The following are some of the results they obtained:

volume of bulb =  $249.8 \text{ cm}^3$

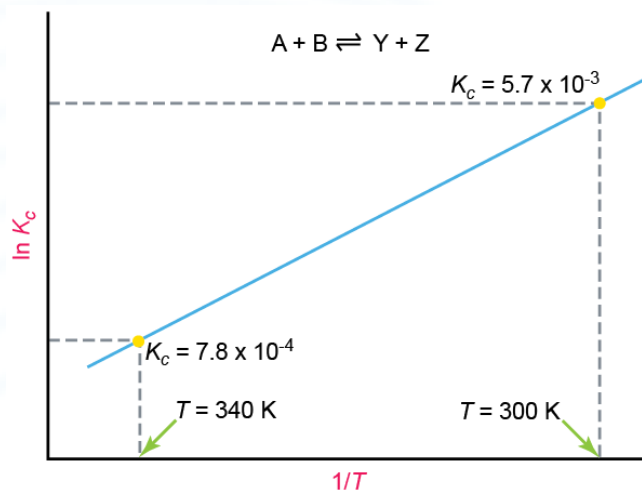
amount of iodine = 1.958 mmol

Temperature/ $^\circ\text{C}$	Pressure/Torr
800	558.0
1000	748.0
1200	1019.2

- Calculate the degree of dissociation at each temperature.
- Calculate  $K_c$  at each temperature, for the process  $\text{I}_2 \rightleftharpoons 2\text{I}$ .
- Calculate  $K_P$  at each temperature.
- Obtain values for  $\Delta H^\circ$  and  $\Delta U^\circ$  at 1000  $^\circ\text{C}$ .
- Calculate  $\Delta G^\circ$  and  $\Delta S^\circ$  at 1000  $^\circ\text{C}$ .

[Solution](#)

- 4.41.** The following diagram shows the variation with temperature of the equilibrium constant  $K_c$  for a reaction. Calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 300 K.



[Solution](#)

- 4.42.** The following values apply to a chemical reaction  $A \rightleftharpoons Z$ :

$$\Delta H^\circ = -85.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -170.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

Assuming these values to be temperature independent, calculate the equilibrium constant for the reaction at 300 K. At what temperature is the equilibrium constant equal to unity?

[Solution](#)

- 4.43.** The equilibrium constant  $K_c$  for the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and phosphate is  $1.66 \times 10^5 \text{ mol dm}^{-3}$  at  $37^\circ\text{C}$ , and  $\Delta H^\circ$  is  $-20.1 \text{ kJ mol}^{-1}$ . Calculate  $\Delta S^\circ$  for the hydrolysis at  $37^\circ\text{C}$ . On the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, calculate  $K_c$  at  $25^\circ\text{C}$ .

[Solution](#)

- 4.44.** A dissociation  $A_2 \rightleftharpoons 2A$  has an equilibrium constant of  $7.2 \times 10^{-5} \text{ mol dm}^{-3}$  at 300 K, and a  $\Delta H^\circ$  value of  $40.0 \text{ kJ mol}^{-1}$ . Calculate the standard entropy change for the reaction at 300 K. (What is its standard state?) If the  $\Delta H^\circ$  and  $\Delta S^\circ$  values for this reaction are temperature independent, at what temperature is the equilibrium constant equal to unity?

[Solution](#)

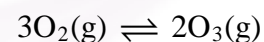
- 4.45.** A reaction  $A + B \rightleftharpoons Z$  has an equilibrium constant of  $4.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$  at 300 K, and a  $\Delta H^\circ$  value of  $-40.2 \text{ kJ mol}^{-1}$ . Calculate the entropy change for the reaction at 300 K. If the  $\Delta H^\circ$  and  $\Delta S^\circ$  values are temperature independent, at what temperature is the equilibrium constant equal to unity?

[Solution](#)

- 4.46.** At 1 bar pressure liquid bromine boils at  $58.2^\circ\text{C}$ , and at  $9.3^\circ\text{C}$  its vapor pressure is 0.1334 bar. Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  to be temperature independent, calculate their values, and calculate the vapor pressure and  $\Delta G^\circ$  at  $25^\circ\text{C}$ .

[Solution](#)

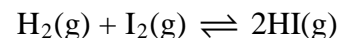
- 4.47.** The standard Gibbs energy of formation of gaseous ozone at  $25^\circ\text{C}$ ,  $\Delta G_f^\circ$ , is  $162.3 \text{ kJ mol}^{-1}$ , for a standard state of 1 bar. Calculate the equilibrium constants  $K_P$ ,  $K_c$ , and  $K_x$  for the process:



What is the mole fraction of  $\text{O}_3$  present at  $25^\circ\text{C}$  at 2 bar pressure?

[Solution](#)

- 4.48.** For the equilibrium:



The following data apply:

$$\Delta H^\circ(300 \text{ K}) = -9.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ(300 \text{ K}) = 22.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

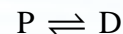
$$\Delta C_p(500 \text{ K}) = -7.11 \text{ J K}^{-1} \text{ mol}^{-1}$$

The latter value can be taken to be the average value between 300 K and 500 K.

Calculate the equilibrium constants  $K_P$ ,  $K_c$ , and  $K_x$  at 500 K. What would be the mole fraction of HI present at equilibrium if HI is introduced into a vessel at 10 atm pressure; how would the mole fraction change with pressure?

[Solution](#)

- \*4.49.** Protein denaturations are usually irreversible but may be reversible under a narrow range of conditions. At pH 2.0, at temperatures ranging from about 40 °C to 50 °C, there is an equilibrium between the active form P and the deactivated form D of the enzyme trypsin:



Thermodynamic values are  $\Delta H^\circ = 283 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 891 \text{ J K}^{-1} \text{ mol}^{-1}$ . Assume these values to be temperature independent over this narrow range, and calculate  $\Delta G^\circ$  and  $K_c$  values at 40.0 °C, 42.0 °C, 44.0 °C, 46.0 °C, 48.0 °C, and 50.0 °C. At what temperature will there be equal concentrations of P and D?

\*\*Note that the high thermodynamic values lead to a considerable change in  $K$  over this 10 °C range.

[Solution](#)

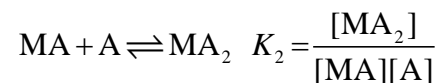
### Binding to Protein Molecules

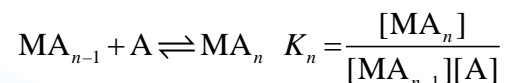
- \*4.50.** Suppose that a large molecule, such as a protein, contains  $n$  sites to which a molecule A (a ligand) can become attached. Assume that the sites are equivalent and independent, so that the reactions  $M + A = MA$ ,  $MA + A = MA_2$ , etc., all have the same equilibrium constant  $K_s$ . Show that the average number of occupied sites per molecule is:

$$\bar{v} = \frac{nK_s[A]}{1 + K_s[A]}$$

[Solution](#)

- \*4.51.** Modify the derivation in Problem 4.50 so as to deal with sites that are not all equivalent; the equilibrium constants for the attachments of successive ligands are each different:





Show that the average number of molecules of A bound per molecule M is:

$$\bar{v} = \frac{K_1[\text{A}] + 2K_1K_2[\text{A}]^2 + \cdots + n(K_1K_2K_3 \cdots K_n)[\text{A}]^n}{1 + K_1[\text{A}] + K_1K_2[\text{A}]^2 + \cdots + (K_1K_2K_3 \cdots K_n)[\text{A}]^n}$$

This equation is important in biology and biochemistry and is often called the *Adair equation*, after the British biophysical chemist G. S. Adair.

[Solution](#)

- \*4.52.** Now show that the Adair equation, derived in Problem 4.51, reduces to the equation obtained in Problem 4.50 when the sites are equivalent and independent. [It is not correct simply to put  $K_1 = K_2 = K_3 \cdots = K_n$ ; certain statistical factors must be introduced. Thus, if  $K_s$  is the equilibrium constant for the binding at a given site,  $K_1 = nK_s$ , since there are  $n$  ways for A to become attached to a given molecule and one way for it to come off. Similarly  $K_2 = (n-1)K_s/2$ ;  $n-1$  ways on and 2 ways off. Continue this argument and develop an expression for  $v$  that will factorize into  $nK_s[\text{A}]/(1 + K_s[\text{A}])$ . Suggest a method of testing the equilibrium obtained and arriving at a value of  $n$  from experimental data.]

[Solution](#)

- \*4.53.** Another special case of the equation derived in Problem 4.51 is if the binding on one site affects that on another. An extreme case is highly cooperative binding, in which the binding of A on one site influences the other sites so that they fill up immediately. This means that  $K_n$  is much greater than  $K_1, K_2$ , etc. Show that now:

$$\bar{v} = \frac{nK[\text{A}]^n}{1 + K[\text{A}]^n}$$

Where  $K$  is the product of  $K_1, K_2, \cdots K_n$ . The British physiologist A. V. Hill suggested that binding problems can be treated by plotting:

$$\ln \frac{\theta}{1-\theta} \quad \text{against} \quad \ln[\text{A}]$$

Where  $\theta$  is the fraction of sites that are occupied. Consider the significance of such *Hill plots*, especially their shapes and slopes, with reference to the equations obtained in Problems 4.50 to 4.53.

[Solution](#)

**Essay Questions**

- 4.54.** Give an account of the effect of temperature on equilibrium constants, and explain how such experimental studies lead to thermodynamic data.
- 4.55.** Give an account of the effect of pressure on (a) the position of equilibrium and (b) the equilibrium constant.
- 4.56.** Explain what experimental studies might be made to decide whether a chemical system is at equilibrium or not.
- 4.57.** Give an account of the coupling of chemical reactions.
- 4.58.** State the Le Chatelier principle, and give several examples.

**\*\*SUGGESTED READING\*\***

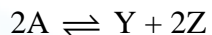
See the listing at the end of Chapter 3. For a discussion of binding problems relating to Problems 4.50–4.53 see:

- K. J. Laidler, *Physical Chemistry with Biological Applications*, Menlo Park, California: Benjamin/Cummings, 1978; especially Section 11.2, “Multiple Equilibria.”
- J. Steinhart, and J. A. Reynolds, *Multiple Equilibria in Proteins*, New York: Academic Press, 1969, especially Chapter 2, “Thermodynamics and Model Systems.”
- C. Tanford, *Physical Chemistry of Macromolecules*, New York: Wiley, 1961, especially Chapter 8, “Multiple Equilibria.”



**Solutions**

**4.1.** A reaction occurs according to the equation



If in a volume of  $5 \text{ dm}^3$  we start with 4 mol of pure A and find that 1 mol of A remains at equilibrium, what is the equilibrium constant  $K_c$ ?

**Solution:**

Given:  $V = 5 \text{ dm}^3$ ,  $n_{\text{initial}} = 4 \text{ mol}$ ,  $n_{\text{equilibrium}} = 1 \text{ mol}$

Required:  $K_c$

This equilibrium problem can be solved using a table:

	2A	$\rightleftharpoons$	Y	+	2Z	
$n_{\text{initial}}$	4		0		0	mol
$n_{\text{equilibrium}}$	1		1.5		3.0	mol
$C_{\text{equilibrium}}$	$\frac{1}{5}$		$\frac{1.5}{5}$		$\frac{3.0}{5}$	$\text{mol dm}^{-3}$

For this reaction,  $K_c$  is given by the equation  $K_c = \frac{[Y][Z]^2}{[A]^2}$ . Solving using the concentrations at equilibrium gives the following,

$$K_c = \frac{\left(\frac{1.5}{5} \text{ mol dm}^{-3}\right)\left(\frac{3.0}{5} \text{ mol dm}^{-3}\right)^2}{\left(\frac{1.0}{5} \text{ mol dm}^{-3}\right)^2}$$

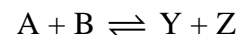
$$\boxed{K_c = 2.7 \text{ mol dm}^{-3}}$$

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## 4.2. The equilibrium constant for a reaction



is 0.1 What amount of A must be mixed with 3 mol of B to yield, at equilibrium, 2 mol of Y?

**Solution:**

Given:  $K_c = 0.1$ ,  $n_{B, \text{initial}} = 3 \text{ mol}$ ,  $n_{Y, \text{equilibrium}} = 2 \text{ mol}$

Required:  $n_{A, \text{initial}}$

This equilibrium problem can be solved using a table:

	A	+	B	$\rightleftharpoons$	Y	+	Z	
$n_{\text{initial}}$	$n_{A, \text{initial}}$		3		0		0	mol
$n_{\text{equilibrium}}$	$n_{A, \text{initial}} - 2$		1		2		2	mol

For this reaction,  $K_c$  is given by the equation  $K_c = \frac{[Y][Z]}{[A][B]}$ . Assuming the total volume is constant for the reaction,  $K_c = \frac{n_Y n_Z}{n_A n_B}$ .

Rearranging for,  $n_A$  gives,  $n_A = \frac{n_Y n_Z}{K_c n_B}$  and therefore  $n_{A, \text{initial}}$  can be determined.

$$n_{A, \text{initial}} - 2 \text{ mol} = \frac{(2 \text{ mol})(2 \cancel{\text{mol}})}{0.1(1 \cancel{\text{mol}})}$$

$$n_{A, \text{initial}} = \frac{(2 \text{ mol})(2 \cancel{\text{mol}})}{0.1(1 \cancel{\text{mol}})} + 2 \text{ mol}$$

$$\boxed{n_{A, \text{initial}} = 42 \text{ mol}}$$

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## 4.3. The equilibrium constant for the reaction



is  $0.25 \text{ dm}^6 \text{ mol}^{-2}$ . In a volume of  $5 \text{ dm}^3$ , what amount of A must be mixed with 4 mol of B to yield 1 mol of Z at equilibrium?

**Solution:**

Given:  $K_c = 0.25 \text{ dm}^6 \text{ mol}^{-2}$ ,  $V = 5 \text{ dm}^3$ ,  $n_{B_{\text{initial}}} = 4 \text{ mol}$ ,  $n_{Z_{\text{equilibrium}}} = 1 \text{ mol}$

Required:  $n_{A_{\text{initial}}}$

This equilibrium problem can be solved using a table:

	A	+	2B	$\rightleftharpoons$	Z	
$n_{\text{initial}}$	$n_{A_{\text{initial}}}$		4		0	mol
$n_{\text{equilibrium}}$	$n_{A_{\text{initial}}} - 1$		2		1	mol
$C_{\text{equilibrium}}$	$\left( \frac{n_{A_{\text{initial}}} - 1}{5} \right)$		$\frac{2}{5}$		$\frac{1}{5}$	$\text{mol dm}^{-3}$

For this reaction,  $K_c$  is given by the equation  $K_c = \frac{[Z]}{[A][B]^2}$ . Rearranging for  $[A]$ , gives,  $[A] = \frac{[Z]}{K_c [B]^2}$  and  $n_{A_{\text{initial}}}$  can be determined from this expression.

$$\frac{(n_{A_{\text{initial}}} - 1) \text{ mol}}{5 \text{ dm}^3} = \frac{\left( \frac{1}{5} \text{ mol dm}^{-3} \right)}{(0.25 \text{ dm}^6 \text{ mol}^{-2}) \left( \frac{2}{5} \text{ mol dm}^{-3} \right)^2}$$

$$\frac{(n_{A_{\text{initial}}} - 1) \text{ mol}}{5 \text{ dm}^3} = 5 \text{ mol dm}^{-3}$$

$$\boxed{n_{A_{\text{initial}}} = 26 \text{ mol}}$$

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4.4. The equilibrium constant  $K_c$  for the reaction



is  $0.0271 \text{ mol dm}^{-3}$  at 1100 K. Calculate  $K_p$  at that temperature.

**Solution:**

Given:  $K_c = 0.0271 \text{ mol dm}^{-3}$ ,  $T = 1100 \text{ K}$

Required:  $K_p$

The relationship between  $K_c$  and  $K_p$  is given by Eq. 4.26,

$K_p = K_c(RT)^{\Sigma v}$  where  $\Sigma v$  is the difference between the moles of products to the moles of reactants.

Since there are three moles of gas produced from two moles of  $\text{SO}_3$ ,

$\Sigma v = +1 \text{ mol}$ .

Solving for  $K_p$  gives,

$$K_p = \left( 0.0271 \text{ mol dm}^{-3} \right) \left( 0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 1100 \text{ K} \right)^{(+1)}$$

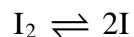
$$K_p = 2.47855 \text{ bar}$$

$$\boxed{K_p = 2.48 \text{ bar}}$$

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4.5. When gaseous iodine is heated, dissociation occurs:



It was found that when 0.0061 mol of iodine was placed in a volume of 0.5 dm<sup>3</sup> at 900 K, the degree of dissociation (the fraction of the iodine that is dissociated) was 0.0274. Calculate  $K_c$  and  $K_P$  at that temperature.

**Solution:**

Given:  $n_{\text{I}_2, \text{initial}} = 0.0061 \text{ mol}$ ,  $V = 0.5 \text{ dm}^3$ ,  $T = 900 \text{ K}$ ,  $\alpha$ , degree of dissociation = 0.0274

Required:  $K_c$  and  $K_P$

This equilibrium problem can be solved using a table:

	$\text{I}_2$	$\rightleftharpoons$	$2\text{I}$	
$n_{\text{initial}}$	0.0061		0	mol
$n_{\text{equilibrium}}$	$0.0061(1 - 0.0274)$		$0.0061 \times 0.0274 \times 2$	
	$= 5.9329 \times 10^{-3}$		$= 3.3428 \times 10^{-4}$	mol

For this reaction,  $K_c$  is given by the equation  $K_c = \frac{[\text{I}]^2}{[\text{I}_2]}$ . Solving using the concentrations at equilibrium gives the following,

$$K_c = \frac{\left( \frac{3.3428 \times 10^{-4}}{0.5} \text{ mol dm}^{-3} \right)^2}{\left( \frac{5.9329 \times 10^{-3}}{0.5} \text{ mol dm}^{-3} \right)}$$

$$K_c = 3.7669 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\boxed{K_c = 3.77 \times 10^{-5} \text{ mol dm}^{-3}}$$

The relationship between  $K_c$  and  $K_P$  is given by Eq. 4.26,

$$K_P = K_c(RT)^{\Sigma v}, \text{ where } \Sigma v \text{ is the difference between the moles of products to the moles of reactants.}$$

Since there are two moles of iodine produced from one mole of iodine gas,

$$\Sigma v = +1 \text{ mol.}$$

Solving for  $K_p$  gives,

$$K_p = \left( 3.77 \times 10^{-5} \text{ mol dm}^{-3} \right) \left( 0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 900 \text{ K} \right)^{(+1)}$$

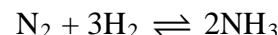
$$K_p = 0.002821 \text{ bar}$$

$$\boxed{K_p = 2.82 \times 10^{-3} \text{ bar}}$$

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**4.6.** It has been observed with the ammonia equilibrium:



that under certain conditions the addition of nitrogen to an equilibrium mixture, *with the temperature and pressure held constant*, causes further dissociation of ammonia. Explain how this is possible. Under what particular conditions would you expect this to occur? Would it be possible for added hydrogen to produce the same effect?

**Solution:**

The equilibrium constant for this reaction is given by,

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{n_{\text{NH}_3}^2}{n_{\text{N}_2} n_{\text{H}_2}^3}$$

If  $n_{\text{N}_2}$  is increased at constant  $V$ , the equilibrium must shift to the right, so as to produce more ammonia. If the *pressure* (as well as the temperature) is kept constant, however, addition of  $\text{N}_2$  requires that  $V$  is increased. If the proportional increase in  $V^2$  is greater than the increase in  $n_{\text{N}_2}$ , the equilibrium will shift to the *left* when  $\text{N}_2$  is added.

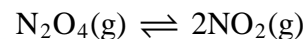
The volume is proportional to  $n_{\text{NH}_3} + n_{\text{N}_2} + n_{\text{H}_2}$  and  $V^2$  is proportional to  $(n_{\text{NH}_3} + n_{\text{N}_2} + n_{\text{H}_2})^2$ . If  $n_{\text{N}_2}$  is much larger than  $n_{\text{NH}_3} + n_{\text{H}_2}$ ,  $V^2$  will increase approximately with  $n_{\text{N}_2}^2$  and therefore increases more strongly than  $n_{\text{N}_2}$ . If  $n_{\text{N}_2}$  is not much larger than  $n_{\text{NH}_3} + n_{\text{H}_2}$ , an increase in  $n_{\text{N}_2}$  will have a relatively small effect on  $V^2$ . The increase in ammonia dissociation when  $\text{N}_2$  is added is therefore expected when  $\text{N}_2$  is in excess, but not otherwise.

On the other hand,  $n_{\text{H}_2}^3$  appears in the equilibrium expression; this varies more strongly than  $V^2$ , and added  $\text{H}_2$  therefore cannot lead to the dissociation of ammonia.

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4.7. Nitrogen dioxide,  $\text{NO}_2$ , exists in equilibrium with dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ :



At  $25.0^\circ\text{C}$  and a pressure of  $0.597\text{ bar}$  the density of the gas is  $1.477\text{ g dm}^{-3}$ . Calculate the degree of dissociation under those conditions, and the equilibrium constants  $K_c$ ,  $K_P$ , and  $K_x$ . What shift in equilibrium would occur if the pressure were increased by the addition of helium gas?

**Solution:**

Given:  $T = 25^\circ\text{C} = 298.15\text{K}$ ,  $P = 0.597\text{ bar}$ ,  $\rho = 1.477\text{ g dm}^{-3}$

Required:  $\alpha$ , degree of dissociation,  $K_c$ ,  $K_P$ , and  $K_x$ . the shift in equilibrium that would occur if the pressure were increased by the addition of helium gas.

To determine the degree of dissociation, we need to first obtain the mole fractions of each gas. First we assume that in  $1\text{ dm}^3$  there are  $n_{\text{N}_2\text{O}_4}$  moles of  $\text{N}_2\text{O}_4$  and  $n_{\text{NO}_2}$  moles of  $\text{NO}_2$ . Therefore the total number of moles is given by  $n = n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}$ .

Using the ideal gas law,  $PV = nRT$ , and solving for  $n$ ,  $n_{\text{N}_2\text{O}_4}$  and  $n_{\text{NO}_2}$  can be obtained.

$$n = \frac{PV}{RT}$$

$$n = \frac{(0.597 \text{ bar})(1 \text{ dm}^3)}{(0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$n = 0.024083 \text{ mol}$$

$$n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} = 0.024083 \text{ mol}$$

The mole fractions can also be determined using the density of the gas given in the problem.

$$\rho = \frac{m}{V} = \frac{M_{\text{N}_2\text{O}_4} n_{\text{N}_2\text{O}_4} + M_{\text{NO}_2} n_{\text{NO}_2}}{V}, \text{ where } m = Mn$$

$$\rho = \frac{(2 \times 14.00674 \text{ g mol}^{-1} + 4 \times 15.9994 \text{ g mol}^{-1}) n_{\text{N}_2\text{O}_4} + (14.00674 \text{ g mol}^{-1} + 2 \times 15.9994 \text{ g mol}^{-1}) n_{\text{NO}_2}}{1 \text{ dm}^3}$$

$$\rho = \frac{(92.01108 \text{ g mol}^{-1}) n_{\text{N}_2\text{O}_4} + (46.00554 \text{ g mol}^{-1}) n_{\text{NO}_2}}{1 \text{ dm}^3}$$

$$\rho = \frac{(46.00554 \text{ g mol}^{-1})(2n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2})}{1 \text{ dm}^3}$$

$$(2n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}) = \frac{(1.477 \text{ g dm}^{-3})(1 \text{ dm}^3)}{(46.00554 \text{ g mol}^{-1})}$$

$$(2n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}) = 0.032105 \text{ mol}$$

Now we have two equations and two unknowns, and therefore we can solve for the mole fractions.

$$n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} = 0.024083 \text{ mol} \quad (1)$$

$$2n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} = 0.032105 \text{ mol} \quad (2)$$

Subtracting (1) from (2) gives,

$$n_{\text{N}_2\text{O}_4} = 0.008022 \text{ mol}$$

$$\boxed{n_{\text{N}_2\text{O}_4} = 8.02 \times 10^{-3} \text{ mol}}$$

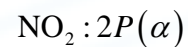
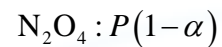
$$n_{\text{NO}_2} = 0.024083 \text{ mol} - 0.008022 \text{ mol}$$

$$n_{\text{NO}_2} = 0.016061 \text{ mol}$$

$$\boxed{n_{\text{NO}_2} = 1.61 \times 10^{-2} \text{ mol}}$$

If the degree of dissociation is  $\alpha$ , the amounts of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  present are:





Since partial pressures are proportional to the number of moles of each species present,

$$n_{\text{N}_2\text{O}_4} \propto P(1-\alpha)$$

$$n_{\text{NO}_2} \propto 2P(\alpha)$$

$$\text{therefore, } \frac{n_{\text{NO}_2}}{n_{\text{N}_2\text{O}_4}} = \frac{2P(\alpha)}{P(1-\alpha)}$$

Solving for  $\alpha$  gives,

$$\frac{(1-\alpha)}{(\alpha)} = \frac{2n_{\text{N}_2\text{O}_4}}{n_{\text{NO}_2}}$$

$$\frac{1}{\alpha} - 1 = \frac{2n_{\text{N}_2\text{O}_4}}{n_{\text{NO}_2}}$$

$$\frac{1}{\alpha} = \frac{2n_{\text{N}_2\text{O}_4}}{n_{\text{NO}_2}} + 1$$

$$\frac{1}{\alpha} = \frac{2n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}}{n_{\text{NO}_2}}$$

$$\alpha = \frac{n_{\text{NO}_2}}{2n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}}$$

$$\alpha = \frac{0.016\ 061\ \text{mol}}{2(0.008\ 022\ \text{mol}) + (0.016\ 061\ \text{mol})}$$

$$\alpha = 0.500\ 265$$

$$\boxed{\alpha = 0.500}$$

The equilibrium constant for this reaction is given by  $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$ . From our assumption that in  $1 \text{ dm}^3$  there are  $n_{\text{N}_2\text{O}_4}$  moles of  $\text{N}_2\text{O}_4$  and  $n_{\text{NO}_2}$  moles of  $\text{NO}_2$ , we can solve for  $K_c$ .

$$K_c = \frac{\left(\frac{0.016\,061 \text{ mol}}{1 \text{ dm}^3}\right)^2}{\left(\frac{0.008\,022 \text{ mol}}{1 \text{ dm}^3}\right)}$$

$$K_c = 0.032\,156 \text{ mol dm}^{-3}$$

$$\boxed{K_c = 0.0322 \text{ mol dm}^{-3}}$$

The relationship between  $K_c$  and  $K_P$  is given by Eq. 4.26,

$K_P = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products.

Since there are two moles of nitrogen dioxide produced from one mole of dinitrogen tetroxide,

$\Sigma v = +1 \text{ mol}$ .

Solving for  $K_P$  gives,

$$K_P = \left(0.032\,156 \cancel{\text{mol dm}^{-3}}\right) \left(0.083145 \cancel{\text{bar dm}^3 \text{K}^{-1} \text{mol}^{-1}} \times 298.15 \cancel{\text{K}}\right)^{(+1)}$$

$$K_P = 0.797\,137 \text{ bar}$$

$$\boxed{K_P = 0.797 \text{ bar}}$$

The relationship between  $K_x$  and  $K_P$  is given by Eq. 4.32,

$K_P = K_x P^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products.

Rearranging for  $K_x$  gives,

$$K_x = K_P P^{-\Sigma v}$$

Since there are two moles of nitrogen dioxide produced from one mole of dinitrogen tetroxide,

$$\Sigma \nu = +1 \text{ mol.}$$

$K_x$  can therefore be solved, giving,

$$K_x = (0.797 \text{ bar})(0.597 \text{ bar})^{-1}$$

$$K_x = 1.335238$$

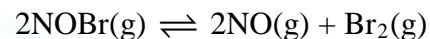
$$\boxed{K_x = 1.34}$$

The addition of helium gas would have no effect on the equilibrium since the concentrations, partial pressures, and mole fractions would remain unchanged.

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4.8. At 25.0 °C the equilibrium:



is rapidly established. When 1.10 g of NOBr is present in a 1.0-dm<sup>3</sup> vessel at 25.0 °C the pressure is 0.355 bar. Calculate the equilibrium constants  $K_P$ ,  $K_c$ , and  $K_x$ .

**Solution:**

Given:  $m = 1.10 \text{ g}$ ,  $V = 1 \text{ dm}^3$ ,  $T = 25^\circ\text{C} = 298.15\text{K}$ ,  $P = 0.355 \text{ bar}$

Required:  $K_P$ ,  $K_c$ , and  $K_x$

The equilibrium constant for this reaction is given by  $K_c = \frac{[\text{NO}]^2 [\text{Br}_2]}{[\text{NOBr}]^2}$ . To calculate  $K_c$ , we must first determine  $n_{\text{NOBr}}$ , the number of moles initially present of NOBr,

$$n_{\text{NOBr}} = \frac{m_{\text{NOBr}}}{M_{\text{NOBr}}}$$

$$n_{\text{NOBr}} = \frac{1.10 \text{ g}}{(14.00674 \text{ g mol}^{-1} + 15.9994 \text{ g mol}^{-1} + 79.904 \text{ g mol}^{-1})}$$

$$n_{\text{NOBr}} = 0.010008 \text{ mol}$$

$$n_{\text{NOBr}} = 0.01 \text{ mol}$$

If  $\alpha$  is the degree of dissociation, then the number of moles of each gas at equilibrium is given in the following table:

	2NOBr	$\rightleftharpoons$	2NO	+	Br <sub>2</sub>	
$n_{\text{initial}}$	0.01		0		0	mol
$n_{\text{equilibrium}}$	$0.01(1-\alpha)$		$0.01\alpha$		$0.01\left(\frac{\alpha}{2}\right)$	mol

The total number of moles is given by  $n = n_{\text{NOBr}} + n_{\text{NO}} + n_{\text{Br}_2}$

$$n = 0.01(1 - \alpha) + 0.01\alpha + 0.01\left(\frac{\alpha}{2}\right)$$

$$n = 0.01 + 0.01\left(\frac{\alpha}{2}\right)$$

$$n = 0.01 + 0.005\alpha$$

Using the ideal gas law,  $PV = nRT$ , and solving for  $n$ ,  $\alpha$  can be obtained

$$n = \frac{PV}{RT}$$

$$n = \frac{(0.355 \text{ bar})(1 \text{ dm}^3)}{(0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$n = 0.01432 \text{ mol}$$

$$\text{where } n = 0.01 + 0.005\alpha$$

$$\alpha = \frac{n - 0.01}{0.005}$$

$$\alpha = \frac{0.01432 \text{ mol} - 0.01}{0.005}$$

$$\alpha = 0.864$$

From  $\alpha$ ,  $n_{\text{NOBr}}$ ,  $n_{\text{NO}}$ , and  $n_{\text{Br}_2}$  can be obtained.

$$n_{\text{NOBr}} = 0.01 \text{ mol}(1 - \alpha)$$

$$n_{\text{NO}} = 0.01 \text{ mol}(\alpha)$$

$$n_{\text{Br}_2} = 0.005 \text{ mol}(\alpha)$$

$$n_{\text{NOBr}} = 0.01 \text{ mol}(1 - 0.864)$$

$$n_{\text{NO}} = 0.01 \text{ mol}(0.864)$$

$$n_{\text{Br}_2} = 0.005 \text{ mol}(0.864)$$

$$n_{\text{NOBr}} = 1.36 \times 10^{-3} \text{ mol}$$

$$n_{\text{NO}} = 8.64 \times 10^{-3} \text{ mol}$$

$$n_{\text{Br}_2} = 4.32 \times 10^{-3} \text{ mol}$$

Solving for  $K_c$  gives,

$$K_c = \frac{\left( \frac{8.64 \times 10^{-3} \text{ mol}}{1 \text{ dm}^3} \right)^2 \left( \frac{4.32 \times 10^{-3} \text{ mol}}{1 \text{ dm}^3} \right)}{\left( \frac{1.36 \times 10^{-3} \text{ mol}}{1 \text{ dm}^3} \right)^2}$$

$$K_c = 0.174 \text{ 35 mol dm}^{-3}$$

$$\boxed{K_c = 0.174 \text{ mol dm}^{-3}}$$

The relationship between  $K_c$  and  $K_p$  is given by Eq. 4.26,

$K_p = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products.

Since there are three moles of total gas produced from two moles of NOBr,

$$\Sigma v = +1 \text{ mol.}$$

Solving for  $K_p$  gives,

$$K_p = \left( 0.174 \text{ 35 mol dm}^{-3} \right) \left( 0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \right)^{(+1)}$$

$$K_p = 4.322 \text{ 08 bar}$$

$$\boxed{K_p = 4.32 \text{ bar}}$$

The relationship between  $K_x$  and  $K_p$  is given by Eq. 4.32,

$K_p = K_x P^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products.

Rearranging for  $K_x$  gives,

$$K_x = K_p P^{-\Sigma v}$$

Since there are three moles of total gas produced from two moles of NOBr,

$$\Sigma v = +1 \text{ mol.}$$

$K_x$  can therefore be solved, giving,

$$K_x = (4.322\,08\,\text{bar})(0.355\,\text{bar})^{-1}$$

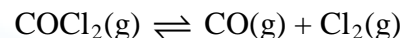
$$K_x = 12.174\,87$$

$$\boxed{K_x = 12.2}$$

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**4.9.** At 100 °C and 2 bar pressure the degree of dissociation of phosgene is  $6.30 \times 10^{-5}$ . Calculate  $K_P$ ,  $K_c$ , and  $K_x$  for the dissociation:



**Solution:**

Given:  $T = 100\text{ }^\circ\text{C} = 373.15\text{ K}$ ,  $P = 2\text{ bar}$ ,  $\alpha = 6.30 \times 10^{-5}$

Required:  $K_P$ ,  $K_c$ , and  $K_x$

The equilibrium constant in terms of partial pressures is given by  $K_P = \frac{P_{\text{CO}} P_{\text{Cl}_2}}{P_{\text{COCl}_2}}$ . To calculate  $K_P$ , we must first determine the partial pressures of each gas present.

If  $\alpha$  is the degree of dissociation, then the partial pressures of each gas at equilibrium is given in the following table:

$\text{COCl}_2$	$\rightleftharpoons$	$\text{CO}$	+	$\text{Cl}_2$	
$P(1-\alpha)$		$P\alpha$		$P\alpha$	bar

The total number pressure is given by  $P_{\text{total}} = P_{\text{COCl}_2} + P_{\text{CO}} + P_{\text{Cl}_2}$

$$P_{\text{total}} = P(1-\alpha) + P\alpha + P\alpha$$

$$P_{\text{total}} = P + P\alpha$$

$$P(1+\alpha) = 2\text{ bar}$$

$$P = \frac{2\text{ bar}}{(1+\alpha)}$$

$$P = \frac{2\text{ bar}}{(1+6.30 \times 10^{-5})}$$

$$P = 1.999\ 87\text{ bar}$$

$$P = 2\text{ bar}$$

Solving for  $K_P$ , we obtain,



$$K_p = \frac{(\cancel{P}\alpha)(P\alpha)}{\cancel{P}(1-\alpha)}$$

$$K_p = \frac{P\alpha^2}{(1-\alpha)}$$

$$K_p = \frac{(2 \text{ bar})(6.30 \times 10^{-5})^2}{(1 - 6.30 \times 10^{-5})}$$

$$K_p = 7.9385 \times 10^{-9} \text{ bar}$$

$$\boxed{K_p = 7.94 \times 10^{-9} \text{ bar}}$$

The relationship between  $K_c$  and  $K_p$  is given by Eq. 4.26,

$K_p = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products. Rearranging for  $K_c$  gives,

$$K_c = K_p(RT)^{-\Sigma v}$$

Since there are two moles of gas produced from one moles of  $\text{COCl}_2$ ,

$$\Sigma v = +1 \text{ mol}$$

Solving for  $K_c$  gives,

$$K_c = (7.9385 \times 10^{-9} \cancel{\text{bar}}) \left( 0.083145 \cancel{\text{bar}} \text{ dm}^3 \cancel{\text{K}^{-1}} \text{ mol}^{-1} \times 373.15 \cancel{\text{K}} \right)^{(-1)}$$

$$K_c = 2.558697 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\boxed{K_c = 2.56 \times 10^{-10} \text{ mol dm}^{-3}}$$

The relationship between  $K_x$  and  $K_p$  is given by Eq. 4.32,

$K_p = K_x P^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products.

Rearranging for  $K_x$  gives,

$$K_x = K_p P^{-\Sigma \nu}$$

Since there are two moles of gas produced from one moles of  $\text{COCl}_2$ ,

$$\Sigma \nu = +1 \text{ mol}$$

$K_x$  can therefore be solved, giving,

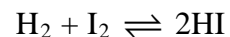
$$K_x = (7.9385 \times 10^{-9} \text{ bar}) (2 \text{ bar})^{-1}$$

$$K_x = 3.96925 \times 10^{-9}$$

$$\boxed{K_x = 3.97 \times 10^{-9}}$$

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**4.10.** In a study of the equilibrium

1 mol of  $\text{H}_2$  and 3 mol of  $\text{I}_2$  gave rise at equilibrium to  $x$  mol of HI. Addition of a further 2 mol of  $\text{H}_2$  gave an additional  $x$  mol of HI. What is  $x$ ? What is  $K$  at the temperature of the experiment?

**Solution:**

Given:  $n_{\text{H}_2} = 1$  mol,  $n_{\text{I}_2} = 3$  mol,  $n_{\text{H}_2 \text{ added}} = 2$  mol

Required:  $x$ ,  $K$

This equilibrium problem can be solved using a table:

	$\text{H}_2$	+	$\text{I}_2$	$\rightleftharpoons$	$2\text{HI}$	
$n_{\text{initial}}$	1		3		0	mol
$n_{\text{equilibrium}}$	$1 - \frac{x}{2}$		$3 - \frac{x}{2}$		$x$	mol
$n_{\text{after H}_2 \text{ added}}$	$3 - x$		$3 - x$		$2x$	mol

For this reaction,  $K$  is given by the equation  $K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$ . Assuming the volume is constant, the expression for  $K$  becomes,  $K = \frac{n_{\text{HI}}^2}{n_{\text{H}_2} n_{\text{I}_2}}$

$K$  is always constant, therefore the two expressions obtained at equilibrium and after  $\text{H}_2$  is added can be used to solve for  $x$ .

$$K = \frac{(\cancel{x})^2}{\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)} = \frac{4\cancel{x}^2}{(3-x)(3-x)}$$

$$(3-x)^2 = 4\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)$$

$$9 - 6x + \cancel{x}^2 = 12 - 8x + \cancel{x}^2$$

$$2x = 3$$

$$\boxed{x = \frac{3}{2}}$$

Substituting for  $x$ ,  $K$  can be solved.

$$K = \frac{4\left(\frac{3}{2}\right)^2}{\left(3 - \frac{3}{2}\right)^2}$$

$$K = \frac{9}{\left(\frac{3}{2}\right)^2}$$

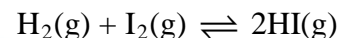
$$K = \frac{9}{\left(\frac{9}{4}\right)}$$

$$\boxed{K = 4}$$

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**4.11.** The equilibrium constant for the reaction below is 20.0 at 40.0 °C:



The vapor pressure of solid iodine is 0.10 bar at that temperature. If 12.7 g of solid iodine are placed in a 10-dm<sup>3</sup> vessel at 40.0 °C, what is the minimum amount of hydrogen gas that must be introduced in order to remove all the solid iodine?

**Solution:**

Given:  $K = 20.0$ ,  $T = 40.0\text{ °C} = 313.15\text{ K}$ ,  $P = 0.10\text{ bar}$ ,  $m = 12.7\text{ g}$ ,  $V = 10\text{ dm}^3$

Required:  $n_{\text{H}_2}$

First, the number of moles of I<sub>2</sub> is given by,

$$n_{\text{I}_2} = \frac{m}{M}$$

$$n_{\text{I}_2} = \frac{12.7\text{ g}}{(2 \times 126.90447\text{ g mol}^{-1})}$$

$$n_{\text{I}_2} = 0.050\,037\,6\text{ mol}$$

$$n_{\text{I}_2} = 0.050\text{ mol}$$

By examining the reaction, the consumption of 0.050 mol of I<sub>2</sub> leads to the formation of 0.10 mol of HI.

The equilibrium constant for this reaction in terms of partial pressures is given by,

$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}P_{\text{I}_2}}, \text{ where } P_{\text{HI}} \text{ is obtained from the ideal gas law.}$$

$$P_{\text{HI}} = \frac{nRT}{V}$$

$$P_{\text{HI}} = \frac{(0.10 \text{ mol})(0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(313.15 \text{ K})}{10 \text{ dm}^3}$$

$$P_{\text{HI}} = 0.26037 \text{ bar}$$

Rearranging and solving for  $P_{\text{H}_2}$  gives,

$$P_{\text{H}_2} = \frac{(0.26037 \text{ bar})^2}{20(0.1 \text{ bar})}$$

$$P_{\text{H}_2} = 0.033896 \text{ bar}$$

Then, if  $P_{\text{H}_2}$  is the partial pressure of  $\text{H}_2$  after equilibrium is established,  $n_{\text{H}_2 \text{ equilibrium}}$  can be obtained using the ideal gas law.

$$n_{\text{H}_2 \text{ equilibrium}} = \frac{P_{\text{H}_2} V}{RT}$$

$$n_{\text{H}_2 \text{ equilibrium}} = \frac{(0.033896 \text{ bar})(10 \text{ dm}^3)}{(0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(313.15 \text{ K})}$$

$$n_{\text{H}_2 \text{ equilibrium}} = 0.013018 \text{ mol}$$

This means 0.013018 mol of  $\text{H}_2$  is produced in the equilibrium mixture, and 0.05 mol of  $\text{H}_2$  is required to remove the 0.05 mol of  $\text{I}_2$ .  $n_{\text{H}_2}$  is therefore equal to 0.013018 mol + 0.05 mol.

$$n_{\text{H}_2} = 0.013018 \text{ mol} + 0.05 \text{ mol}$$

$$n_{\text{H}_2} = 0.063018 \text{ mol}$$

$$\boxed{n_{\text{H}_2} = 0.063 \text{ mol}}$$

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**4.12.** The degree of dissociation  $\alpha$  of  $\text{N}_2\text{O}_4(\text{g})$  is 0.483 at 0.597 bar and 0.174 at 6.18 bar. The temperature is 298 K for both measurements. Calculate  $K_P$ ,  $K_c$ , and  $K_x$  in each case.

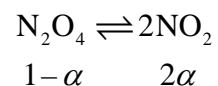
(Hint: See Example 4.1.)

**Solution:**

Given:  $\alpha_{P=0.597 \text{ bar}} = 0.483$ ,  $\alpha_{P=6.18 \text{ bar}} = 0.174$ ,  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:  $K_P$ ,  $K_c$ , and  $K_x$  in each case

Suppose that we start with 1 mol of  $\text{N}_2\text{O}_4$  and that  $\alpha$  mol have become converted into  $\text{NO}_2$ ; the amounts at equilibrium are



The total amount is given by,  $1-\alpha+2\alpha=1+\alpha$ . If  $P$  is the total pressure, the partial pressures are

$$\text{N}_2\text{O}_4 : \frac{1-\alpha}{1+\alpha}P \quad \text{and} \quad \text{NO}_2 : \frac{2\alpha}{1+\alpha}P$$

The equilibrium constant in terms of partial pressures is given by  $K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$

Solving for  $K_P$ , we obtain,

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 P^2}{\left(\frac{1-\alpha}{1+\alpha}\right) P}$$

$$K_p = P \frac{4\alpha^2}{(1+\alpha)^2} \left( \frac{1+\cancel{\alpha}}{1-\alpha} \right)$$

$$K_p = P \frac{4\alpha^2}{(1+\alpha)(1-\alpha)}$$

$$K_p = P \frac{4\alpha^2}{1-\alpha^2}$$

At  $P = 0.597$  bar ,

$$K_p = (0.597 \text{ bar}) \frac{4(0.483)^2}{1-(0.483)^2}$$

$$K_p = 0.726 \text{ 60 bar}$$

$$\boxed{K_p = 0.727 \text{ bar}}$$

At  $P = 6.18$  bar ,

$$K_p = (6.18 \text{ bar}) \frac{4(0.174)^2}{1-(0.174)^2}$$

$$K_p = 0.771 \text{ 79 bar}$$

$$\boxed{K_p = 0.772 \text{ bar}}$$

The relationship between  $K_c$  and  $K_p$  is given by Eq. 4.26,

$K_p = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products. Rearranging for  $K_c$  gives,

$$K_c = K_p(RT)^{-\Sigma v}$$



Since there are two moles of nitrogen dioxide produced from one mole of dinitrogen tetroxide,

$$\Sigma \nu = +1 \text{ mol.}$$

Solving for  $K_c$  at  $P = 0.597$  bar gives,

$$K_c = (0.726 \text{ 60 bar}) \left( 0.083 \text{ 145 } \cancel{\text{bar}} \text{ dm}^3 \cancel{\text{K}}^{-1} \text{ mol}^{-1} \times 298.15 \cancel{\text{K}} \right)^{(-1)}$$

$$K_c = 0.029 \text{ 31 mol dm}^{-3}$$

$$\boxed{K_c = 2.93 \times 10^{-2} \text{ mol dm}^{-3}}$$

Solving for  $K_c$  at  $P = 6.18$  bar gives,

$$K_c = (0.771 \text{ 79 bar}) \left( 0.083 \text{ 145 } \cancel{\text{bar}} \text{ dm}^3 \cancel{\text{K}}^{-1} \text{ mol}^{-1} \times 298.15 \cancel{\text{K}} \right)^{(-1)}$$

$$K_c = 0.031 \text{ 13 mol dm}^{-3}$$

$$\boxed{K_c = 3.11 \times 10^{-2} \text{ mol dm}^{-3}}$$

The relationship between  $K_x$  and  $K_P$  is given by Eq. 4.32,

$$K_P = K_x P^{\Sigma \nu}, \text{ where } \Sigma \nu \text{ is the difference between the moles of products to the moles of reactants.}$$

Rearranging for  $K_x$  gives,

$$K_x = K_P P^{-\Sigma \nu}$$

Since there are two moles of nitrogen dioxide produced from one mole of dinitrogen tetroxide,

$$\Sigma \nu = +1 \text{ mol.}$$

Solving for  $K_x$  at  $P = 0.597$  bar gives,

$$K_x = (0.726\ 60\ \cancel{\text{bar}})(0.597\ \cancel{\text{bar}})^{-1}$$

$$K_x = 1.217\ 09$$

$$\boxed{K_x = 1.22}$$

Solving for  $K_x$  at  $P = 6.18\ \text{bar}$  gives,

$$K_x = (0.771\ 79\ \cancel{\text{bar}})(6.18\ \cancel{\text{bar}})^{-1}$$

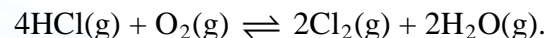
$$K_x = 0.124\ 89$$

$$\boxed{K_x = 0.125}$$

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**4.13.** One mole of HCl mixed with oxygen is brought into contact with a catalyst until the following equilibrium has been established:



If  $y$  mol of  $\text{HCl}$  is formed, derive an expression for  $K_P$  in terms of  $y$  and the partial pressure of oxygen.

(Hint: First develop expressions for the ratios  $x_{\text{Cl}_2}/x_{\text{HCl}}$  and  $x_{\text{H}_2\text{O}}/x_{\text{Cl}_2}$  in terms of  $y$  and  $P_{\text{O}_2}$ .)

**Solution:**

Given:  $n_{\text{HCl}} = 1$  mol

Required:  $K_P$  in terms of  $y$  and  $P_{\text{O}_2}$

Rewriting the reaction in terms of one mole of HCl gives,



From examining the equation above, it is possible to establish the following relationships:

$$\frac{x_{\text{Cl}_2}}{x_{\text{HCl}}} = \frac{y}{2(1-y)}, \text{ and } \frac{x_{\text{H}_2\text{O}}}{x_{\text{Cl}_2}} = 1$$

These ratios also hold for partial pressures and solving for  $K_P$ ,

$$K_p = \frac{(P_{\text{Cl}_2})^{\frac{1}{2}} (P_{\text{H}_2\text{O}})^{\frac{1}{2}}}{(P_{\text{HCl}})(P_{\text{O}_2})^{\frac{1}{4}}}$$

$$K_p = \frac{P_{\text{Cl}_2}}{P_{\text{HCl}} (P_{\text{O}_2})^{\frac{1}{4}}}$$

$$K_p = \frac{y}{2(1-y)} \times \frac{1}{(P_{\text{O}_2})^{\frac{1}{4}}}$$

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**4.14.** Using the result of Problem 4.13, evaluate  $K_P$  for an experiment in which 49% HCl and 51% O<sub>2</sub> are brought into contact with a catalyst until the reaction is complete at 1 bar and 480 °C. The fraction of HCl converted per mole is found to be 0.76.

**Solution:**

Given: 49% HCl, 51% O<sub>2</sub>,  $P = 1$  bar,  $T = 480$  °C = 753.15 K,  $y = 0.76$

Required:  $K_P$

The result from problem 4.13 gives  $K_P$  as.

$$K_P = \frac{y}{2(1-y)} \times \frac{1}{(P_{O_2})^{\frac{1}{4}}}$$

Solving using  $P_{O_2} = 0.51 \times 1$  bar

$$K_P = \frac{0.76}{2(1-0.76)} \times \frac{1}{(0.51 \text{ bar})^{\frac{1}{4}}}$$

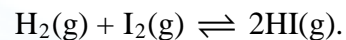
$$K_P = 1.873 \text{ 61 bar}^{-\frac{1}{4}}$$

$$\boxed{K_P = 1.9 \text{ bar}^{-\frac{1}{4}}}$$

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- 4.15.** 10.0 g of HI is introduced into an evacuated vessel at 731 K and allowed to reach equilibrium. Find the mole fractions of  $\text{H}_2$ ,  $\text{I}_2$ , and HI present at equilibrium.  $K_P = K_c = K_x = 65.0$  for the reaction



(Hint: see Example 4.2)

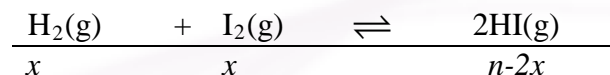
**Solution:**

Given:  $m_{\text{HI}} = 10.0 \text{ g}$ ,  $T = 731 \text{ K}$ ,  $K_P = K_c = K_x = 65.0$

Required:  $x_{\text{H}_2}$ ,  $x_{\text{I}_2}$ ,  $x_{\text{HI}}$

Note first that because the reaction involves no change in the number of molecules, the volume of the vessel is irrelevant, since it cancels out in the equilibrium equation. Note also that from Eq. 4.26 and Eq. 4.32 the equilibrium constants  $K_P$ ,  $K_c$ , and  $K_x$  are all the same and that they are dimensionless.

Since there are no reactants present initially, we can write,



Where  $n$  is the initial amount of HI present,

$$n_{\text{HI}} = \frac{m}{M}$$

$$n_{\text{HI}} = \frac{10.0 \text{ g}}{(1.00794 \text{ g mol}^{-1} + 126.90447 \text{ g mol}^{-1})}$$

$$n_{\text{HI}} = 0.078178 \text{ mol}$$

$$n_{\text{HI}} = 7.8179 \times 10^{-2} \text{ mol}$$

The equilibrium constant for this reaction in terms of partial pressures is given by,

$$K_P = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}}, \text{ which can be written in terms of moles as,}$$

$$K_p = \frac{n_{\text{HI}}^2}{n_{\text{H}_2} n_{\text{I}_2}}$$

Solving for the  $x$ , the mole fractions  $x_{\text{H}_2}$ ,  $x_{\text{I}_2}$ ,  $x_{\text{HI}}$  can be obtained.

$$K_p = \frac{(n-2x)^2}{(x)(x)}$$

$$65.0 = \frac{(n-2x)^2}{x^2}$$

$$\sqrt{65.0} = \frac{(n-2x)}{x}$$

$$\sqrt{65.0} = \frac{n}{x} - 2$$

$$8.062\ 26 + 2 = \frac{7.8179 \times 10^{-2} \text{ mol}}{x}$$

$$x = \frac{7.8179 \times 10^{-2} \text{ mol}}{10.062\ 26}$$

$$x = 7.7695 \times 10^{-3} \text{ mol}$$

The mole fractions are given by the expressions,

$$x_{\text{H}_2} = x_{\text{I}_2} = \frac{x}{n}, \text{ and } x_{\text{HI}} = \frac{n-2x}{n}$$

Solving for  $x_{\text{H}_2}$ ,  $x_{\text{I}_2}$ , and  $x_{\text{HI}}$  gives,

$$x_{\text{H}_2} = x_{\text{I}_2} = \frac{7.7695 \times 10^{-3} \cancel{\text{mol}}}{7.8179 \times 10^{-2} \cancel{\text{mol}}}$$

$$x_{\text{H}_2} = x_{\text{I}_2} = 0.099\,381$$

$$x_{\text{H}_2} = x_{\text{I}_2} = 9.94 \times 10^{-2}$$

$$x_{\text{HI}} = \frac{7.8179 \times 10^{-2} \cancel{\text{mol}} - 2 \times 7.7695 \times 10^{-3} \cancel{\text{mol}}}{7.8179 \times 10^{-2} \cancel{\text{mol}}}$$

$$x_{\text{HI}} = 0.080\,124$$

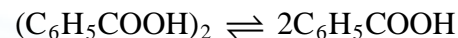
$$x_{\text{HI}} = 8.01 \times 10^{-2}$$

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**4.16.** The equilibrium constant for the reaction



in benzene solution at 10 °C is  $2.19 \times 10^{-3} \text{ mol dm}^{-3}$ .

**a.** Calculate  $\Delta G^\circ$  for the dissociation of the dimer.

**b.** If 0.1 mol of benzoic acid is present in 1 dm<sup>3</sup> of benzene at 10 °C, what are the concentrations of the monomer and of the dimer?

**Solution:**

Given:  $T = 10.0 \text{ }^\circ\text{C} = 283.15 \text{ K}$ ,  $K = 2.19 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $n = 0.1 \text{ mol}$ ,  $V = 1 \text{ dm}^{-3}$

Required:  $\Delta G^\circ$ ,  $C_{\text{monomer}}$ ,  $C_{\text{dimer}}$

**a.** Solving for  $\Delta G^\circ$ , given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c$

$$\Delta G^\circ = (-8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(283.15 \text{ K}) \ln(2.19 \times 10^{-3} \text{ mol dm}^{-3})$$

$$\Delta G^\circ = 14\,417 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 14.4 \text{ kJ mol}^{-1}}$$

**b.** This equilibrium problem can be solved using a table:

	$(\text{C}_6\text{H}_5\text{COOH})_2$	$\rightleftharpoons$	$2\text{C}_6\text{H}_5\text{COOH}$	
$C_{\text{initial}}$	0		0.1	$\text{mol dm}^{-3}$
$C_{\text{equilibrium}}$	$x$		$0.1 - 2x$	$\text{mol dm}^{-3}$

The equilibrium constant for this reaction is given by,

$$K_c = \frac{[\text{C}_6\text{H}_5\text{COOH}]^2}{[(\text{C}_6\text{H}_5\text{COOH})_2]}$$

Using the concentrations at equilibrium given in the table,  $x$  can be obtained.

$$2.19 \times 10^{-3} = \frac{(0.1 - 2x)^2}{x}$$

$$0.01 - 0.40219x + 4x^2 = 0$$

Using the quadratic formula, the expression can be further simplified.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{0.40219 \pm \sqrt{(-0.40219)^2 - 4(4)(0.01)}}{2(4)}$$

$$x = \frac{0.40219 \pm 0.041914}{8}$$

$$x = 0.055513 \text{ mol dm}^{-3} \text{ or } x = 0.0450345 \text{ mol dm}^{-3}$$

From the equilibrium concentrations, we know that there are  $(0.1 - 2x) \text{ mol dm}^{-3}$  of  $\text{C}_6\text{H}_5\text{COOH}$ , therefore, we take  $x = 0.0450345$  since  $2x$  cannot be greater than 0.1.

Therefore,

$$C_{\text{monomer}} = 0.045\,034\,5 \text{ mol dm}^{-3}$$

$$C_{\text{monomer}} = 5 \times 10^{-2} \text{ mol dm}^{-3}$$

$$C_{\text{dimer}} = 0.1 \text{ mol dm}^{-3} - 2(0.045\,034\,5 \text{ mol dm}^{-3})$$

$$C_{\text{dimer}} = 0.009\,931 \text{ mol dm}^{-3}$$

$$C_{\text{dimer}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$$

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**4.17.** At 3000 K the equilibrium partial pressures of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  are 0.6, 0.4, and 0.2 atm, respectively. Calculate  $\Delta G^\circ$  at 3000 K for the reaction:



**Solution:**

Given:  $T = 3000 \text{ K}$ ,  $P_{\text{CO}_2} = 0.6 \text{ atm}$ ,  $P_{\text{CO}} = 0.4 \text{ atm}$ ,  $P_{\text{O}_2} = 0.2 \text{ atm}$

Required:  $\Delta G^\circ$

$\Delta G^\circ$  is given by Eq. 4.20 as  $\Delta G^\circ = -RT \ln K_p^\circ$

The equilibrium constant for this reaction is given by

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{O}_2}}{P_{\text{CO}_2}^2}$$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -RT \ln \left( \frac{P_{\text{CO}}^2 P_{\text{O}_2}}{P_{\text{CO}_2}^2} \right)$$

$$\Delta G^\circ = (-8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(3000 \text{ K}) \ln \left( \frac{(0.4 \text{ atm})^2 (0.2 \text{ atm})}{(0.6 \text{ atm})^2} \right)$$

$$\Delta G^\circ = 60\,372.45 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 6 \times 10 \text{ kJ mol}^{-1}}$$

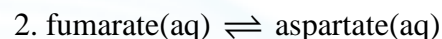
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**4.18.** The conversion of malate into fumarate:



is endergonic at body temperature, 37 °C;  $\Delta G^\circ$  is 2.93 kJ mol<sup>-1</sup>. In metabolism the reaction is coupled with



for which  $\Delta G^\circ$  is -15.5 kJ mol<sup>-1</sup> at 37 °C.

- Calculate  $K_c$  for reaction 1.
- Calculate  $K_c$  for reaction 2.
- Calculate  $K_c$  and  $\Delta G^\circ$  for the coupled reaction 1 + 2.

**Solution:**

Given:  $T_1 = 37^\circ\text{C} = 310.15 \text{ K}$ ,  $\Delta G_1^\circ = 2.93 \text{ kJ mol}^{-1}$

$T_2 = 37^\circ\text{C} = 310.15 \text{ K}$ ,  $\Delta G_2^\circ = -15.5 \text{ kJ mol}^{-1}$

Required  $K_{c1}$ ,  $K_{c2}$ ,  $K_{c1+2}$ ,  $\Delta G_{1+2}^\circ$

a. The relationship between  $\Delta G^\circ$  and  $K_c$  is given by Eq. 4.27,

$$\Delta G^\circ = -RT \ln K_c^\circ$$

Rearranging and solving for  $K_c$  gives,

$$\ln K_c^\circ = \frac{-\Delta G^\circ}{RT}$$

$$K_c^\circ = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_{c1} = e^{\frac{-2.93 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(310.15 \text{ K})}}$$

$$K_{c1} = 0.321 \text{ 03}$$

$$\boxed{K_{c1} = 0.321}$$

b. Using the procedure in part a,  $K_{c2}$  can be obtained.

$$K_{c2} = e^{\frac{-(-15.5 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(310.15 \text{ K})}}$$

$$K_{c2} = 407.761$$

$$\boxed{K_{c2} = 408}$$

c. The coupled reaction of 1 + 2 is given by,



$K_{c1+2}$  is given by Eq. 4.65,

$$K_1 K_2 = K_3$$

Therefore solving for  $K_{c1+2}$  gives,

$$K_{c1+2} = K_{c1} \times K_{c2}$$

$$K_{c1+2} = 0.321 \times 408$$

$$K_{c1+2} = 130.968$$

$$\boxed{K_{c1+2} = 131}$$

$\Delta G_{1+2}^\circ$  is given by Eq. 4.67, the sum of the free energies of each reaction

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

Solving for  $\Delta G_{1+2}^\circ$  gives,

$$\Delta G_{1+2}^\circ = 2.93 \text{ kJ mol}^{-1} - 15.5 \text{ kJ mol}^{-1}$$

$$\Delta G_{1+2}^\circ = -12.57 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G_{1+2}^\circ = -12.6 \text{ kJ mol}^{-1}}$$

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**4.19.** From the data in Appendix D, deduce the  $\Delta G^\circ$  and  $K_P$  values for the following reactions at 25.0 °C:

- a.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- b.  $2\text{H}_2(\text{g}) + \text{C}_2\text{H}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g})$
- c.  $\text{H}_2(\text{g}) + \text{C}_2\text{H}_4(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g})$
- d.  $2\text{CH}_4(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$

**Solution:**

Given:  $T = 25^\circ\text{C} = 298.15 \text{ K}$ , Appendix D

Required:  $\Delta G^\circ$  and  $K_P$  for a-d

a. From Eq. 3.91 the Gibbs energies of formation can be used to obtain  $\Delta G^\circ$  for each reaction.

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = 2(-16.4 \text{ kJ mol}^{-1}) - (0 + 3(0))$$

$$\boxed{\Delta G^\circ = -32.8 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$  and  $K_P$  is given by Eq. 4.20,

$$\Delta G^\circ = -RT \ln K_P$$

Rearranging and solving for  $K_P$  gives,

$$\ln K_P = \frac{-\Delta G^\circ}{RT}$$

$$K_P = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_P = e^{\frac{-(-32.8 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_P = 557\,552 \text{ bar}^{-2}$$

$$\boxed{K_P = 5.58 \times 10^5 \text{ bar}^{-2}}$$

b. Using the same procedure as part a,

$$\Delta G^\circ = (-32.0 \text{ kJ mol}^{-1}) - (2(0) + 209.9 \text{ kJ mol}^{-1})$$

$$\Delta G^\circ = -241.9 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G^\circ = -242 \text{ kJ mol}^{-1}}$$

$$K_p = e^{\frac{-(-241.9 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_p = 2.392\,522 \times 10^{42} \text{ bar}^{-2}$$

$$\boxed{K_p = 2.39 \times 10^{42} \text{ bar}^{-2}}$$

c. Using the same procedure as part a,

$$\Delta G^\circ = (-32.0 \text{ kJ mol}^{-1}) - ((0) + 68.4 \text{ kJ mol}^{-1})$$

$$\Delta G^\circ = -100.4 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G^\circ = -100 \text{ kJ mol}^{-1}}$$

$$K_p = e^{\frac{-(-100 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_p = 3.304\,94 \times 10^{17} \text{ bar}^{-1}$$

$$\boxed{K_p = 3.30 \times 10^{17} \text{ bar}^{-1}}$$

d. Using the same procedure as part a,

$$\Delta G^\circ = (-32.0 \text{ kJ mol}^{-1} + (0)) - 2(-50.5 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta G^\circ = 69 \text{ kJ mol}^{-1}}$$

$$K_p = e^{\frac{-(69 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_p = 8.161\,64 \times 10^{-13}$$

$$\boxed{K_p = 8.2 \times 10^{-13}}$$

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**4.20.** Calculate  $K_c$  and  $K_x$  for each of the reactions in Problem 4.19 assuming total pressures of 1 bar in each case.

**Solution:**

Given:  $P = 1$  bar, Problem 4.19

Required:  $K_c$ , and  $K_x$  in each case

The relationship between  $K_c$  and  $K_P$  is given by Eq. 4.26,  $K_P = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products. Rearranging for  $K_c$  gives,

$$K_c = K_P(RT)^{-\Sigma v}$$

Since there are two moles of ammonia produced from one mole of nitrogen gas and three moles of hydrogen gas,

$$\Sigma v = -2 \text{ mol.}$$

Solving for  $K_c$ ,

$$K_c = \left(5.58 \times 10^5 \cancel{\text{bar}^{-2}}\right) \left(0.083145 \cancel{\text{bar}} \text{ dm}^3 \cancel{\text{K}^{-1}} \text{ mol}^{-1} \times 298.15 \cancel{\text{K}}\right)^{(-2)}$$

$$K_c = 908.013 \text{ mol}^2 \text{ dm}^{-6}$$

$$\boxed{K_c = 9.08 \times 10^2 \text{ mol}^2 \text{ dm}^{-6}}$$

The relationship between  $K_x$  and  $K_P$  is given by Eq. 4.32,

$$K_P = K_x P^{\Sigma v}, \text{ where } \Sigma v \text{ is the difference between the moles of products to the moles of products.}$$

Rearranging for  $K_x$  gives,

$$K_x = K_P P^{-\Sigma v}$$

Since there are two moles of ammonia produced from one mole of nitrogen gas and three moles of hydrogen gas,

$$\Sigma v = -2 \text{ mol.}$$

Solving for  $K_x$

$$K_x = (5.58 \times 10^5 \text{ bar}^{-2}) (1 \text{ bar})^{-2}$$

$$\boxed{K_x = 5.58 \times 10^5}$$

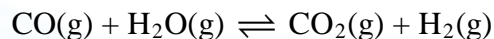
Repeating this procedure for each reaction gives the following results:

	$K_P$	$\Sigma \nu$	$K_c = K_P(RT)^{-\Sigma \nu}$	$K_x = K_P P^{-\Sigma \nu}$
a.	$5.58 \times 10^5 \text{ bar}^{-2}$	-2	$9.08 \times 10^2 \text{ mol}^2 \text{ dm}^{-6}$	$5.58 \times 10^5$
b.	$2.39 \times 10^{42} \text{ bar}^{-2}$	-2	$3.89 \times 10^{39} \text{ mol}^2 \text{ dm}^{-6}$	$2.39 \times 10^{42}$
c.	$3.30 \times 10^{17} \text{ bar}^{-1}$	-1	$1.33 \times 10^{16} \text{ mol dm}^{-3}$	$3.30 \times 10^{17}$
d.	$8.2 \times 10^{-13}$	0	$8.2 \times 10^{-13}$	$8.2 \times 10^{-13}$

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**4.21.** At 25.0 °C the equilibrium constant for the reaction:



is  $1.00 \times 10^{-5}$ , and  $\Delta S^\circ$  is  $41.8 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**a.** Calculate  $\Delta G^\circ$  and  $\Delta H^\circ$  at 25.0 °C.

**b.** Suppose that 2 mol of CO and 2 mol of H<sub>2</sub>O are introduced into a 10-dm<sup>3</sup> vessel at 25.0 °C. What are the amounts of CO, H<sub>2</sub>O, CO<sub>2</sub>, and H<sub>2</sub> at equilibrium?

**Solution:**

Given:  $T = 25^\circ\text{C} = 298.15 \text{ K}$ ,  $K = 1.00 \times 10^{-5}$ ,  $\Delta S^\circ = 41.8 \text{ J K}^{-1} \text{ mol}^{-1}$

$n_{\text{CO}} = 2 \text{ mol}$ ,  $n_{\text{H}_2\text{O}} = 2 \text{ mol}$ ,  $V = 10 \text{ dm}^3$

Required:  $\Delta G^\circ$ ,  $\Delta H^\circ$  at 25.0 °C and,  $n_{\text{CO equilibrium}}$ ,  $n_{\text{H}_2\text{O equilibrium}}$ ,  $n_{\text{CO}_2 \text{ equilibrium}}$ ,  $n_{\text{H}_2 \text{ equilibrium}}$

**a.** The relationship between  $\Delta G^\circ$  and  $K$  is given by

$$\Delta G^\circ = -RT \ln K$$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(298.15 \text{ K}\right)\ln\left(1.00 \times 10^{-5}\right)$$

$$\Delta G^\circ = 28\,540 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 2.85 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$  and  $\Delta H^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S,$$

$$\text{Hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta H^\circ$  gives,

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

$$\Delta H^\circ = 28\,540 \text{ J mol}^{-1} + (298.15 \text{ K})(41.8 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta H^\circ = 41\,002 \text{ J mol}^{-1}$$

$$\boxed{\Delta H^\circ = 41.0 \text{ kJ mol}^{-1}}$$

b. This equilibrium problem can be solved using a table:

	CO(g)	+	H <sub>2</sub> O(g)		CO <sub>2</sub> (g)	+	H <sub>2</sub> (g)	
	$\rightleftharpoons$							
$n_{\text{initial}}$	2		2		0		0	mol
$n_{\text{equilibrium}}$	$2 - x$		$2 - x$		$x$		$x$	mol

For this reaction, the equilibrium constant is given by the equation  $K_c = K_p = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$ .

The total volume is constant for the reaction, and cancels out, therefore we can write,

$$K_c = K_p = \frac{n_{\text{CO}_2} n_{\text{H}_2}}{n_{\text{CO}} n_{\text{H}_2\text{O}}}$$

Solving for  $x$ , we can then obtain  $n_{\text{CO equilibrium}}$ ,  $n_{\text{H}_2\text{O equilibrium}}$ ,  $n_{\text{CO}_2 \text{ equilibrium}}$ , and  $n_{\text{H}_2 \text{ equilibrium}}$

$$K_c = K_p = \frac{(x)(x)}{(2-x)(2-x)}$$

$$1.00 \times 10^{-5} = \frac{x^2}{(2-x)^2}$$

$$\sqrt{10^{-5}}(2-x) = x$$

$$2\sqrt{10^{-5}} = x + \sqrt{10^{-5}}x$$

$$2\sqrt{10^{-5}} = x(1 + \sqrt{10^{-5}})$$

$$x = \frac{2\sqrt{10^{-5}}}{(1 + \sqrt{10^{-5}})}$$

$$x = 0.006\,304\,6$$

Therefore,

$$n_{\text{CO}_2 \text{ equilibrium}} = n_{\text{H}_2 \text{ equilibrium}} = x$$

$$n_{\text{CO}_2 \text{ equilibrium}} = n_{\text{H}_2 \text{ equilibrium}} = 0.006\,304\,6$$

$$n_{\text{CO}_2 \text{ equilibrium}} = n_{\text{H}_2 \text{ equilibrium}} = 6.30 \times 10^{-3}$$

$$n_{\text{CO equilibrium}} = n_{\text{H}_2\text{O equilibrium}} = 2 - x$$

$$n_{\text{CO equilibrium}} = n_{\text{H}_2\text{O equilibrium}} = 2 - 0.006\,304\,6$$

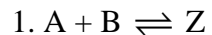
$$n_{\text{CO equilibrium}} = n_{\text{H}_2\text{O equilibrium}} = 1.993\,695\,4$$

$$n_{\text{CO equilibrium}} = n_{\text{H}_2\text{O equilibrium}} = 1.99$$

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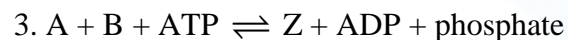
4.22. Suppose that there is a biological reaction:



for which the  $\Delta G^\circ$  value at  $37.0^\circ\text{C}$  is  $23.8\text{ kJ mol}^{-1}$ . (Standard state =  $1\text{ mol dm}^{-3}$ .) Suppose that an enzyme couples this reaction with



for which  $\Delta G^\circ = -31.0\text{ kJ mol}^{-1}$ . Calculate the equilibrium constant at  $37.0^\circ\text{C}$  for these two reactions and for the coupled reaction



**Solution:**

Given:  $\Delta G_1^\circ = 23.8\text{ kJ mol}^{-1}$ ,  $\Delta G_2^\circ = -31.0\text{ kJ mol}^{-1}$ ,

$$T = 37.0^\circ\text{C} = 310.15\text{ K}, n = 1\text{ mol}, V = 1\text{ dm}^{-3}$$

Required:  $K_1, K_2, K_3$

For this reaction,  $K_c$  is given by the equation  $K_c = \frac{[Z]}{[A][B]}$ . Therefore the units of  $K_c$  will be in  $\text{mol}^{-1}\text{ dm}^3$ . The relationship between  $\Delta G^\circ$  and  $K_c$  is given by Eq. 4.27,

$$\Delta G^\circ = -RT \ln K_c^\circ$$

Rearranging and solving for  $K_c$  gives,

$$\ln K_c = \frac{-\Delta G^\circ}{RT}$$

$$K_c = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_1 = e^{\frac{-23.8 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(310.15 \text{ K})}}$$

$$K_1 = 9.812 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\boxed{K_1 = 9.81 \times 10^{-5} \text{ mol dm}^{-3}}$$

$K_2$  can be obtained by following the same procedure.  $K_c$  is given by  $K_c = \frac{[\text{ADP}][\text{phosphate}]}{[\text{ATP}]}$ . Therefore the units of  $K_c$  will be in  $\text{mol dm}^{-3}$

$$K_2 = e^{\frac{-(-31.0 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(310.15 \text{ K})}}$$

$$K_2 = 166\,269 \text{ mol dm}^{-3}$$

$$\boxed{K_2 = 1.66 \times 10^5 \text{ mol dm}^{-3}}$$

For the coupled reaction,  $K_3$  is given by Eq. 4.65,

$$K_1 K_2 = K_3$$

Solving for  $K_3$  gives,

$$K_3 = (9.81 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3) (1.66 \times 10^5 \text{ mol dm}^{-3})$$

$$K_3 = 16.2846$$

$$\boxed{K_3 = 16.3}$$

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**4.23.** The equilibrium between citrate and isocitrate involves *cis*-aconitate as an intermediate:



At 25 °C and pH 7.4 it was found that the molar composition of the mixture was:

90.9%	citrate
2.9%	<i>cis</i> -aconitate
6.2%	isocitrate

Calculate the equilibrium constants for the individual reactions, and for the overall reaction, and  $\Delta G^\circ$  for the citrate-isocitrate system.

**Solution:**

Given:  $T = 25^\circ\text{C} = 298.15\text{ K}$ ,  $\text{pH} = 7.4$ ,  $x_{\text{citrate}} = 0.909$ ,  $x_{\text{cis-aconitate}} = 0.029$ ,  $x_{\text{isocitrate}} = 0.062$

Required:  $K_1$ ,  $K_2$ ,  $K_3$ ,  $\Delta G^\circ$

The individual reactions are given by,

1.  $\text{citrate} \rightleftharpoons \text{cis-aconitate} + \text{H}_2\text{O}$
2.  $\text{cis-aconitate} + \text{H}_2\text{O} \rightleftharpoons \text{isocitrate}$
3.  $\text{citrate} \rightleftharpoons \text{cis-aconitate} + \text{H}_2\text{O} \rightleftharpoons \text{isocitrate}$

$K_1$  is given by the equation  $K_1 = \frac{x_{\text{cis-aconitate}} x_{\text{H}_2\text{O}}}{x_{\text{citrate}}}$ .

Solving for  $K_1$  gives,

$$K_1 = \frac{x_{\text{cis-aconitate}} x_{\text{H}_2\text{O}}}{x_{\text{citrate}}}$$

where  $x_{\text{H}_2\text{O}} = 1$

$$K_1 = \frac{0.029}{0.909} = 0.031\,903\,2$$

$$\boxed{K_1 = 3.19 \times 10^{-2}}$$

$$K_2 \text{ is given by the equation } K_2 = \frac{x_{\text{isocitrate}}}{x_{\text{cis-aconitate}} x_{\text{H}_2\text{O}}}$$

Solving for  $K_2$  gives,

$$K_1 = \frac{x_{\text{cis-aconitate}} x_{\text{H}_2\text{O}}}{x_{\text{citrate}}}$$

where  $x_{\text{H}_2\text{O}} = 1$

$$K_2 = \frac{0.062}{0.029} = 2.137\,93$$

$$\boxed{K_2 = 2.14}$$

$K_3$  is the overall rate constant and is given by Eq. 4.65,

$$K_1 K_2 = K_3$$

Solving for  $K_3$  gives,

$$K_3 = (3.190\,32 \times 10^{-2})(2.137\,92)$$

$$K_3 = 0.068\,207$$

$$\boxed{K_3 = 6.82 \times 10^{-2}}$$

The relationship between  $\Delta G^\circ$  and  $K$  is given by,

$$\Delta G^\circ = -RT \ln K$$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1}\right)\left(298.15 \text{ } \cancel{\text{K}}\right) \ln (0.068207)$$

$$\Delta G^\circ = 6656.545 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 6.66 \text{ kJ mol}^{-1}}$$

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**4.24.** The solubility product of  $\text{Cr}(\text{OH})_3$  is  $3.0 \times 10^{-29} \text{ mol}^4 \text{ dm}^{-12}$  at  $25^\circ\text{C}$ . What is the solubility of  $\text{Cr}(\text{OH})_3$  in water at this temperature?

**Solution:**

Given:  $K_{\text{sp}} = 3.0 \times 10^{-29} \text{ mol}^4 \text{ dm}^{-12}$   $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required: solubility of  $\text{Cr}(\text{OH})_3$

When  $\text{Cr}(\text{OH})_3$  dissolves, the reaction becomes



Where  $a$  is the solubility in  $\text{mol dm}^3$

$K_{\text{sp}}$  is given by the  $K_{\text{sp}} = a(3a)^3 = 27a^4$ .

Solving for  $a$ ,

$$a = \sqrt[4]{\frac{K_{\text{sp}}}{27}}$$

$$a = \sqrt[4]{\frac{(3.0 \times 10^{-29} \text{ mol}^4 \text{ dm}^{-12})}{27}}$$

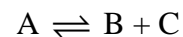
$$a = 3.24668 \times 10^{-8} \text{ mol dm}^{-3}$$

$$\boxed{a = 3.2 \times 10^{-8} \text{ mol dm}^{-3}}$$

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4.25. A gas reaction:



is endothermic and its equilibrium constant  $K_p$  is 1 bar at 25 °C.

- What is  $\Delta G^\circ$  at 25 °C (standard state: 1 bar)?
- Is  $\Delta S^\circ$ , with the same standard state, positive or negative?
- For the standard state of 1 M, what are  $K_c$  and  $\Delta G^\circ$ ?
- Will  $K_p$  at 40 °C be greater than or less than 1 bar?
- Will  $\Delta G^\circ$  at 40 °C (standard state: 1 bar) be positive or negative?

**Solution:**

Given:  $K_p = 1 \text{ bar}$ ,  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:

- a.  $\Delta G^\circ$  is given by Eq. 4.20,  $\Delta G^\circ = -RT \ln K_p^\circ$

$$\Delta G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(298.15 \text{ K}\right) \ln (1 \text{ bar})$$

$$\boxed{\Delta G^\circ = 0 \text{ J mol}^{-1}}$$

- b. The relationship between  $\Delta G^\circ$  and  $\Delta H^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta G^\circ = 0$$

$$\Delta S^\circ = \frac{\Delta H^\circ}{T}$$

Since the reaction is endothermic,

$$\Delta H^\circ > 0$$

$$\therefore \Delta S^\circ > 0$$

c. The relationship between  $K_c$  and  $K_P$  is given by Eq. 4.26,

$K_P = K_c(RT)^{\Sigma \nu}$ , where  $\Sigma \nu$  is the difference between the moles of products to the moles of reactants. Rearranging for  $K_c$  gives,

$$K_c = K_P(RT)^{-\Sigma \nu}$$

Since there are two moles of gas produced from one mole of A,

$$\Sigma \nu = +1 \text{ mol.}$$

Solving for  $K_c$  at  $P = 1 \text{ bar}$  gives,

$$K_c = (1 \text{ bar}) \left( 0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \right)^{(-1)}$$

$$K_c = 0.0403394 \text{ mol dm}^{-3}$$

$$K_c = 4.03 \times 10^{-2} \text{ mol dm}^{-3}$$

$\Delta G^\circ$  is given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c^\circ$

$$\Delta G^\circ = -RT \ln K_c^\circ$$

$$\Delta G^\circ = - \left( 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \right) \ln \left( 4.03394 \times 10^{-2} \text{ mol dm}^{-3} \right)$$

$$\Delta G^\circ = 7958.545 \text{ J mol}^{-1}$$

$$\Delta G^\circ = 7.96 \text{ kJ mol}^{-1}$$

d. Since the reaction is endothermic, increasing the temperature to  $40^\circ\text{C}$ , will shift the equilibrium to the right, making the forward reaction more likely to occur, and the equilibrium constant,  $K_P$ , will increase.

$$K_P > 1 \text{ bar}$$

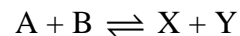
e. Since the reaction is endothermic, increasing the temperature to 40 °C, will shift the equilibrium to the right, making the forward reaction more likely to occur.

$$\Delta G^\circ < 0$$

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**4.26.** A solution reaction:



is endothermic, and  $K_c$  at 25 °C is 10.

- Is the formation of X + Y exergonic at 25 °C?
- Will raising the temperature increase the equilibrium yield of X + Y?
- Is  $\Delta S^\circ$  positive or negative?

**Solution:**

Given:  $K_c = 10$ ,  $T = 25^\circ\text{C} = 298.15\text{ K}$

Required:

- An exergonic reaction is one that releases energy, i.e.,  $\Delta G^\circ < 0$

$\Delta G^\circ$  is given by Eq. 4.27,

$$\Delta G^\circ = -RT \ln K_c$$

$$\Delta G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}\right) \ln(10)$$

$$\Delta G^\circ = -5708.035 \text{ J mol}^{-1}$$

$$\Delta G^\circ = -5.7 \text{ kJ mol}^{-1}$$

Therefore  $\Delta G^\circ$  is less than zero, and the formation of X + Y is exergonic at 25 °C.

- Since the reaction is endothermic, increasing the temperature will shift the equilibrium to the right, making the forward reaction more likely to occur, and the equilibrium yield will increase.

- The relationship between  $\Delta G^\circ$  and  $\Delta H^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,



$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

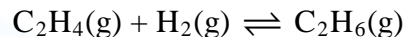
where  $\Delta G^\circ < 0$  and  $\Delta H^\circ < 0$  for an endothermic process,

$$\boxed{\Delta S^\circ > 0}$$

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4.27. From the data given in Appendix D, for the reaction:



Calculate the following:

- $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 25 °C; what is the standard state?
- $K_P$  at 25 °C.
- $K_c$  at 25 °C (standard state: 1 *M*).
- $\Delta G^\circ$  at 25 °C (standard state: 1 *M*).
- $\Delta S^\circ$  at 25 °C (standard state: 1 *M*).
- $K_P$  at 100 °C, on the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent.

**Solution:**

Given: Appendix D,  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:

- a. From Eq. 3.91 the Gibbs energies of formation can be used to obtain  $\Delta G^\circ$  for each reaction.

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = (-32.0 \text{ kJ mol}^{-1}) - (68.4 \text{ kJ mol}^{-1} + (0))$$

$$\Delta G^\circ = -100.4 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G^\circ = -100 \text{ kJ mol}^{-1}}$$

From Eq. 2.53 the enthalpies of formation can be used to obtain  $\Delta H^\circ$  for each reaction.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = (-84.0 \text{ kJ mol}^{-1}) - (52.4 \text{ kJ mol}^{-1} + (0))$$

$$\Delta H^\circ = -136.4 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -136 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{-136.4 \times 10^3 \text{ J mol}^{-1} - (-100.4 \times 10^3 \text{ J mol}^{-1})}{298.15 \text{ K}}$$

$$\Delta S^\circ = -120.744 \text{ J mol}^{-1} \text{ K}$$

$$\boxed{\Delta S^\circ = -121 \text{ J mol}^{-1} \text{ K}}$$

b. The relationship between  $K_p$  and  $\Delta G^\circ$  is given by Eq. 4.20,  $\Delta G^\circ = -RT \ln K_p^\circ$ . Rearranging and solving for  $K_p$  gives,

$$\ln K_p = \frac{-\Delta G^\circ}{RT}$$

$$K_p = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_p = e^{\frac{-(-100.4 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_p = 3.883 \text{ } 65 \times 10^{17} \text{ bar}^{-1}$$

$$\boxed{K_p = 3.88 \times 10^{17} \text{ bar}^{-1}}$$

c. The relationship between  $K_c$  and  $K_p$  is given by Eq. 4.26,

$K_p = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products. Rearranging for  $K_c$  gives,

$$K_c = K_p(RT)^{-\Sigma v}$$

Since there is one mole of gas produced from two moles of gas reactants,

$$\Sigma v = -1 \text{ mol.}$$

Solving for  $K_c$  gives,

$$K_c = (3.883\,65 \times 10^{17} \text{ bar}^{-1}) (0.083\,145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})^{(-1)}$$

$$K_c = 9.627\,44 \times 10^{18} \text{ dm}^3 \text{ mol}^{-1}$$

$$\boxed{K_c = 9.63 \times 10^{18} \text{ dm}^3 \text{ mol}^{-1}}$$

d. The relationship between  $K_c$  and  $\Delta G^\circ$  is given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K}) \ln (9.627\,44 \times 10^{18} \text{ dm}^3 \text{ mol}^{-1})$$

$$\Delta G^\circ = -108\,358 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -108 \text{ kJ mol}^{-1}}$$

e. Solving for  $\Delta S^\circ$  using the expression obtained in part a. gives,

$$\Delta S^\circ = \frac{-136.4 \times 10^3 \text{ J mol}^{-1} - (-108\,358 \text{ J mol}^{-1})}{298.15 \text{ K}}$$

$$\Delta S^\circ = -94.051\,49 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\boxed{\Delta S^\circ = -94.1 \text{ J mol}^{-1} \text{ K}^{-1}}$$

f. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, we solve for  $K_p$ ,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ(100^\circ\text{C}) = -136.4 \times 10^3 \text{ J mol}^{-1} - (373.15 \text{ K})(-120.744 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$\Delta G^\circ = -91\,462.268 \text{ J mol}^{-1}$$

$$K_p = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_p(100^\circ\text{C}) = e^{\frac{-(-91\,462.268 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K})}}$$

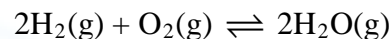
$$K_p = 6.351\,13 \times 10^{12} \text{ bar}^{-1}$$

$$\boxed{K_p = 6.35 \times 10^{12} \text{ bar}^{-1}}$$

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4.28. From the data in Appendix D, for the reaction:



Calculate the following:

- $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 25 °C (standard state: 1 bar).
- $K_P$  at 25 °C.
- $\Delta G^\circ$  and  $K_P$  at 2000 °C, on the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent.

**Solution:**

Given: Appendix D,  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:

- a. From Eq. 3.91 the Gibbs energies of formation can be used to obtain  $\Delta G^\circ$  for the reaction.

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = 2(-228.6 \text{ kJ mol}^{-1}) - (2(0) + (0))$$

$$\boxed{\Delta G^\circ = -457.2 \text{ kJ mol}^{-1}}$$

From Eq. 2.53 the enthalpies of formation can be used to obtain  $\Delta H^\circ$  for each reaction.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = 2(-241.826 \text{ kJ mol}^{-1}) - (2(0) + (0))$$

$$\boxed{\Delta H^\circ = -483.652 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$  and  $\Delta H^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{-483.652 \times 10^3 \text{ J mol}^{-1} - (-457.2 \times 10^3 \text{ J mol}^{-1})}{298.15 \text{ K}}$$

$$\Delta S^\circ = -88.720 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\boxed{\Delta S^\circ = -88.72 \text{ J mol}^{-1} \text{ K}^{-1}}$$

b. The relationship between  $K_p$  and  $\Delta G^\circ$  is given by Eq. 4.20,  $\Delta G^\circ = -RT \ln K_p$ . Rearranging and solving for  $K_p$  gives,

$$\ln K_p = \frac{-\Delta G^\circ}{RT}$$

$$K_p = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_p = e^{\frac{-(-457.2 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_p = 1.252 \text{ } 03 \times 10^{80} \text{ bar}^{-1}$$

$$\boxed{K_p = 1.252 \times 10^{80} \text{ bar}^{-1}}$$

c. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, we solve for  $\Delta G^\circ$  and  $K_p$  at 2000 °C.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ(2000^\circ\text{C}) = -483.652 \times 10^3 \text{ J mol}^{-1} - (2273.15 \text{ K})(-88.720 44 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$\Delta G^\circ = -281 977.1318 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -282.0 \text{ kJ mol}^{-1}}$$

$$K_p = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_p(2000^\circ\text{C}) = e^{\frac{-(-281 977.1318 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(2273.15 \text{ K})}}$$

$$K_p = 3 015 697.02 \text{ bar}^{-1}$$

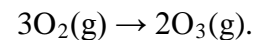
$$\boxed{K_p = 3.016 \times 10^6 \text{ bar}^{-1}}$$

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**4.29.** Calculate the equilibrium constant at 400 K for the reaction:



where  $\Delta_f G^\circ(\text{O}_3, \text{g}) = 163.2 \text{ kJ mol}^{-1}$ .

**Solution:**

Given:  $T = 400 \text{ K}$ ,  $\Delta_f G^\circ(\text{O}_3, \text{g}) = 163.2 \text{ kJ mol}^{-1}$

Required:  $K$

From Eq. 3.91 the Gibbs energies of formation can be used to obtain  $\Delta G^\circ$  for the reaction.

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = 2(163.2 \text{ kJ mol}^{-1}) - 3(0)$$

$$\Delta G^\circ = 326.4 \text{ kJ mol}^{-1}$$

The relationship between  $K$  and  $\Delta G^\circ$  is given by  $\Delta G^\circ = -RT \ln K_p^\circ$ . Rearranging and solving for  $K$  gives,

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K = e^{\frac{-(326.4 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(400 \text{ K})}}$$

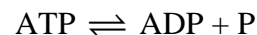
$$K = 2.38538 \times 10^{-43}$$

$$\boxed{K = 2.39 \times 10^{-43}}$$

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**4.30.** The hydrolysis of adenosine triphosphate to give adenosine diphosphate and phosphate can be represented by:



The following values have been obtained for the reaction at 37 °C (standard state: 1 *M*):

$$\Delta G^\circ = -31.0 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -20.1 \text{ kJ mol}^{-1}$$

- Calculate  $\Delta S^\circ$ .
- Calculate  $K_c$  at 37 °C.
- On the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, calculate  $\Delta G^\circ$  and  $K_c$  at 25 °C.

**Solution:**

Given:  $T = 37^\circ\text{C} = 313.15 \text{ K}$ ,  $\Delta G^\circ = -31.0 \text{ kJ mol}^{-1}$ ,  $\Delta H^\circ = -20.1 \text{ kJ mol}^{-1}$

Required:

a. The relationship between  $\Delta G^\circ$  and  $\Delta H^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{-20.1 \times 10^3 \text{ J mol}^{-1} - (-31.0 \times 10^3 \text{ J mol}^{-1})}{313.15 \text{ K}}$$

$$\Delta S^\circ = 35.144 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\boxed{\Delta S^\circ = 35.1 \text{ J mol}^{-1} \text{ K}^{-1}}$$

b. The relationship between  $K_c$  and  $\Delta G^\circ$  is given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c$ . Rearranging and solving for  $K_c$  gives,

$$\ln K_c = \frac{-\Delta G^\circ}{RT}$$

$$K_c = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_c = e^{\frac{-(-31.0 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(310.15 \text{ K})}}$$

$$K_c = 166269.3995 \text{ mol dm}^{-3}$$

$$\boxed{K_c = 1.66 \times 10^5 \text{ mol dm}^{-3}}$$

c. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, we solve for  $\Delta G^\circ$  and  $K_c$  at 25 °C.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ(25^\circ\text{C}) = -20.1 \times 10^3 \text{ J mol}^{-1} - (298.15 \text{ K})(35.14429 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$\Delta G^\circ = -30\,578.270\,06 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -30.6 \text{ kJ mol}^{-1}}$$

$$K_c = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_c(25^\circ\text{C}) = e^{\frac{-(-30\,578.270\,06 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_c = 227\,539.635 \text{ mol dm}^{-3}$$

$$\boxed{K_c = 2.28 \times 10^5 \text{ mol dm}^{-3}}$$

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**4.31.** Thermodynamic data for *n*-pentane(g) and neo-pentane(g) (standard state: 1 bar and 25 °C) are as follows:

Compound	Enthalpy of Formation, $\Delta H_f^\circ$ kJ mol <sup>-1</sup>	Entropy, $S^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>
<i>n</i> -Pertane(g)	- 146.44	349.0
Neopentane(g)	- 165.98	306.4

**a.** Calculate  $\Delta G^\circ$  for *n*-pentane → neopentane.

**b.** Pure *n*-pentane is in a vessel at 1 bar and 25 °C, and a catalyst is added to bring about the equilibrium between *n*-pentane and neopentane. Calculate the final partial pressures of the two isomers.

**Solution:**

a. The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

To obtain  $\Delta G^\circ$  we must first determine  $\Delta H^\circ$  and  $\Delta S^\circ$ .

From Eq. 2.53 the enthalpies of formation can be used to obtain  $\Delta H^\circ$  for each reaction.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = (-165.98 \text{ kJ mol}^{-1}) - (-146.44 \text{ kJ mol}^{-1})$$

$$\Delta H^\circ = -19.54 \text{ kJ mol}^{-1}$$

From Eq. 3.69 the absolute entropies can be used to obtain  $\Delta S^\circ$  for each reaction.

$$\Delta S = \sum S(\text{products}) - \sum S(\text{reactants})$$

$$\Delta S = 306.4 \text{ J K}^{-1} \text{ mol}^{-1} - 349.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S = -42.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

Solving for  $\Delta G^\circ$ ,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ(100^\circ\text{C}) = -19.54 \times 10^3 \text{ J mol}^{-1} - (298.15 \text{ K})(-42.6 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$\Delta G^\circ = -6838.81 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -6.84 \text{ kJ mol}^{-1}}$$

b. To calculate the partial pressures, we need to obtain the equilibrium constant  $K_p$ . The relationship between  $K_p$  and  $\Delta G^\circ$  is given by Eq. 4.20,  $\Delta G^\circ = -RT \ln K_p$ . Rearranging and solving for  $K_p$  gives,

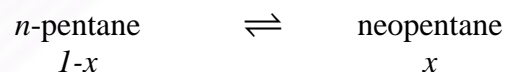
$$K_p = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_p(100^\circ\text{C}) = e^{\frac{-(-6838.81 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_p = 15.779 \text{ bar}^{-1}$$

The expression for  $K_p$  is given by,  $K_p = \frac{P_{\text{neopentane}}}{P_{n\text{-pentane}}}$

At equilibrium, we have



Therefore  $K_p$  becomes,  $K_p = \frac{x}{1-x}$ . Solving for  $x$ , we can obtain the partial pressures.

$$K_p(1-x) = x$$

$$K_p - K_px - x = 0$$

$$K_p - x(K_p + 1) = 0$$

$$x(K_p + 1) = K_p$$

$$x = \frac{K_p}{(K_p + 1)}$$

$$x = \frac{15.779\,83}{(15.779\,83 + 1)}$$

$$x = 0.940\,405\text{ bar}$$

$$P_{\text{neopentane}} = x = 0.940\text{ bar}$$

$$P_{n\text{-pentane}} = (1-x) = 1\text{ bar} - 0.940\,405\text{ bar}$$

$$P_{n\text{-pentane}} = 0.059\,595\text{ bar}$$

$$P_{n\text{-pentane}} = 0.060\text{ bar}$$

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**4.32. a.** An equilibrium constant  $K_c$  is increased by a factor of 3 when the temperature is raised from 25.0 °C to 40.0 °C. Calculate the standard enthalpy change.

**b.** What is the standard enthalpy change if instead  $K_c$  is *decreased* by a factor of 3 under the same conditions?

**Solution:**

Given:  $T_1 = 25.0^\circ\text{C} = 298.15\text{ K}$ ,  $T_2 = 40.0^\circ\text{C} = 313.15\text{ K}$

Required:  $\Delta H^\circ$

a. The problem states that  $K_{c2} = (3K_{c1})$ . To obtain  $\Delta H^\circ$ , the standard enthalpy change, we use Eq.4.83.

$$\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta U^\circ}{R}$$

This can be written as,  $\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta H^\circ}{R}$  since  $\Delta U^\circ$  and  $\Delta H^\circ$  are very close in solution.

Rearranging and solving for  $\Delta H^\circ$  gives,

$$\Delta H^\circ = -R \left( \frac{d \ln K_c^\circ}{d(1/T)} \right)$$

$$\Delta H^\circ = -R \left( \ln \left( \frac{K_{c2}}{K_{c1}} \right) \div \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1} \right) \left( \ln \left( \frac{3 \cancel{K_{c1}}}{\cancel{K_{c1}}} \right) \div \left( \frac{1}{313.15 \cancel{\text{K}}} - \frac{1}{298.15 \cancel{\text{K}}} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J mol}^{-1} \right) \left( \ln(3) \div (-1.606\,586\,19 \times 10^{-4}) \right)$$

$$\Delta H^\circ = 56\,856.033\,83 \text{ J mol}^{-1}$$

$$\boxed{\Delta H^\circ = 56.9 \text{ kJ mol}^{-1}}$$

b. The problem states that  $K_{c2} = \left(\frac{1}{3} K_{c1}\right)$ . Using the same procedure as part a.,  $\Delta H^\circ$  can be obtained.

$$\Delta H^\circ = -R \left( \ln \left( \frac{K_{c2}}{K_{c1}} \right) \div \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1} \right) \left( \ln \left( \frac{\cancel{K_{c1}}}{3\cancel{K_{c1}}} \right) \div \left( \frac{1}{313.15 \cancel{\text{K}}} - \frac{1}{298.15 \cancel{\text{K}}} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J mol}^{-1} \right) \left( \ln \left( \frac{1}{3} \right) \div \left( -1.606\,586\,19 \times 10^{-4} \right) \right)$$

$$\Delta H^\circ = -56\,856.033\,83 \text{ J mol}^{-1}$$

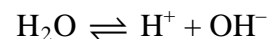
$$\boxed{\Delta H^\circ = -56.9 \text{ kJ mol}^{-1}}$$

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**4.33. a.** The ionic product  $[H^+][OH^-]$ , which is the equilibrium constant for the dissociation of water;



is  $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at  $25.0^\circ\text{C}$  and  $1.45 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at  $30.0^\circ\text{C}$ . Deduce  $\Delta H^\circ$  and  $\Delta S^\circ$  for the process.

**b.** Calculate the value of the ionic product at body temperature ( $37^\circ\text{C}$ ).

**Solution:**

Given:  $K_1 = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ ,  $T_1 = 25.0^\circ\text{C} = 298.15 \text{ K}$   $K_2 = 1.45 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ ,  $T_2 = 30.0^\circ\text{C} = 303.15 \text{ K}$

Required:

a. To obtain  $\Delta H^\circ$ , the standard enthalpy change, we use Eq.4.83.  $\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta U^\circ}{R}$

This can be written as,  $\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta H^\circ}{R}$  since  $\Delta U^\circ$  and  $\Delta H^\circ$  are very close in solution.

Rearranging and solving for  $\Delta H^\circ$  gives,

$$\Delta H^\circ = -R \left( \frac{d \ln K_c^\circ}{d(1/T)} \right)$$

$$\Delta H^\circ = -R \left( \ln \left( \frac{K_2}{K_1} \right) \div \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1} \right) \left( \ln \left( \frac{1.45 \times 10^{-14} \cancel{\text{mol}^2} \cancel{\text{dm}^{-6}}}{1.00 \times 10^{-14} \cancel{\text{mol}^2} \cancel{\text{dm}^{-6}}} \right) \div \left( \frac{1}{303.15 \cancel{\text{K}}} - \frac{1}{298.15 \cancel{\text{K}}} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J mol}^{-1} \right) \left( \ln(1.45) \div (-5.531942 \times 10^{-5}) \right)$$

$$\Delta H^\circ = 55\,845.943\,25 \text{ J mol}^{-1}$$

$$\boxed{\Delta H^\circ = 55.8 \text{ kJ mol}^{-1}}$$

To obtain  $\Delta S^\circ$  we use the relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

To continue to solve, we must determine  $\Delta G^\circ$ . The relationship between  $K$  and  $\Delta G^\circ$  is given by  $\Delta G^\circ = -RT \ln K$ .

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1}\right)(298.15 \text{ } \cancel{\text{K}}) \ln(1.00 \times 10^{14} \text{ mol}^2 \text{ dm}^{-6})$$

$$\Delta G^\circ = -79\,912.492\,32 \text{ J mol}^{-1}$$

Solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{55\,845.943\,25 \text{ J mol}^{-1} - (-79\,912.492\,32 \text{ J mol}^{-1})}{298.15 \text{ K}}$$

$$\Delta S^\circ = -80.719\,60 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\boxed{\Delta S^\circ = -80.7 \text{ J mol}^{-1} \text{ K}^{-1}}$$

b. To obtain  $K$  at  $37^\circ\text{C}$  we use Eq.4.83.  $\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta U^\circ}{R}$

This can be written as,  $\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta H^\circ}{R}$  since  $\Delta U^\circ$  and  $\Delta H^\circ$  are very close in solution.

Rearranging and solving for  $K_2$ , the solubility product at  $37^\circ\text{C}$ , gives,

$$\ln\left(\frac{K_2}{K_1}\right) \div \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\frac{\Delta H^\circ}{R}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_2 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln K_1$$

$$K_2 = e^{\left(-\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln K_1\right)}$$

Solving for  $K_2$ ,

$$K_2 = e^{\left(-\frac{\left(55\,845.943\,25\,\cancel{\text{J}}\,\text{mol}^{-1}\right)}{\left(8.3145\,\cancel{\text{J}}\,\cancel{\text{K}}^{-1}\,\text{mol}^{-1}\right)} \left(\frac{1}{310.15\,\text{K}} - \frac{1}{298.15\,\text{K}}\right) + \ln\left(1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}\right)\right)}$$

$$K_2 = e^{\left(-\left(6716.692\,916\right)\left(-1.297701 \times 10^{-4}\right) + \left(-32.236\,19\right)\right)}$$

$$K_2 = e^{\left(-31.364\,564\,09\right)}$$

$$K_2 = 2.390\,798 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$$

$$\boxed{K_2 = 2.39 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}}$$

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**4.34.** The equilibrium constant  $K_P$  for the reaction  $\text{I}_2(\text{g}) + \text{cyclopentane}(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}) + \text{cyclopentadiene}(\text{g})$  varies with temperatures according to the equation:

$$\log_{10}(K_P/\text{bar}) = 7.55 - 4844/(T/\text{K})$$

- Calculate  $K_P$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  (standard state: 1 bar) at 400 °C.
- Calculate  $K_c$  and  $\Delta G^\circ$  (standard state: 1 M) at 400 °C.
- If  $\text{I}_2$  and cyclopentane are initially at 400 °C and at concentrations of 0.1 M, calculate the final equilibrium concentrations of  $\text{I}_2$ , cyclopentane, HI, and cyclopentadiene.

**Solution:**

Given:  $T = 400^\circ\text{C} = 673.15 \text{ K}$

Required:

a.  $K_P$  can be obtained from the equation  $\log_{10}(K_P/\text{bar}) = 7.55 - 4844/(T/\text{K})$ .

$$\log_{10}(K_P / \text{bar}) = 7.55 - \frac{4844}{(T / \text{K})}$$

$$K_P = 10^{\left(7.55 - \frac{4844}{T}\right)}$$

$$K_P = 10^{\left(7.55 - \frac{4844}{673.15}\right)}$$

$$K_P = 2.259 \text{ 34 bar}^{-1}$$

$$\boxed{K_P = 2.26 \text{ bar}^{-1}}$$

The relationship between  $K_P$  and  $\Delta G^\circ$  is given by Eq. 4.20,  $\Delta G^\circ = -RT \ln K_P^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(673.15 \text{ K}\right) \ln\left(2.259 \text{ 34 bar}^{-1}\right)$$

$$\Delta G^\circ = -4561.885 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -4.56 \text{ kJ mol}^{-1}}$$

The temperature dependence of the equilibrium constant is given by the equation

$$\log_{10}(K_P/\text{bar}) = 7.55 - 4844/(T/\text{K}). \text{ From this equation, } \Delta H^\circ, \text{ by converting it into Eq. 4.75, } \ln K_P^\circ = -\frac{\Delta H^\circ}{RT} + I.$$

To convert  $\log_{10} K_P$  to  $\ln K_P$ , we use the law of logarithm that states  $\log_a (b^{\log_b x}) = \log_a x$

$$\ln(10^{\log_{10} K_P}) = \ln K_P$$

$$\ln K_P = 2.303 \log_{10} K_P$$

$$2.303 \log_{10} K_P = \left( -\frac{4844}{T} \right) 2.303 + 7.55$$

To solve for  $\Delta H^\circ$ , we drop the 7.55 term and multiply by  $R$

$$\Delta H^\circ = 2.303 R \log_{10} K_P$$

$$\Delta H^\circ = 2.303 (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (4844 \text{ K})$$

$$\Delta H^\circ = 92754.334 \text{ J mol}^{-1}$$

$$\boxed{\Delta H^\circ = 92.75 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{92754.334 \text{ J mol}^{-1} - (-4561.885 \text{ J mol}^{-1})}{673.15 \text{ K}}$$

$$\Delta S^\circ = 144.568 \text{ J mol}^{-1} \text{ K}$$

$$\boxed{\Delta S^\circ = 145 \text{ J mol}^{-1} \text{ K}}$$

b. The relationship between  $K_c$  and  $K_p$  is given by Eq. 4.26,

$K_p = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products. Rearranging for  $K_c$  gives,

$$K_c = K_p(RT)^{-\Sigma v}$$

Since there are three moles produced from two moles of gas reactants,

$$\Sigma v = +1 \text{ mol.}$$

Solving for  $K_c$  gives,

$$K_c = \left( 2.259 \text{ 34 bar}^{-1} \right) \left( 0.083 \text{ 145 bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 673.15 \text{ K} \right)^{-(+1)}$$

$$K_c = 0.040 \text{ 368 dm}^3 \text{ mol}^{-1}$$

$$\boxed{K_c = 4.04 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}}$$

The relationship between  $K_c$  and  $\Delta G^\circ$  is given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = - \left( 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) \left( 673.15 \text{ K} \right) \ln \left( 0.040 \text{ 368 dm}^3 \text{ mol}^{-1} \right)$$

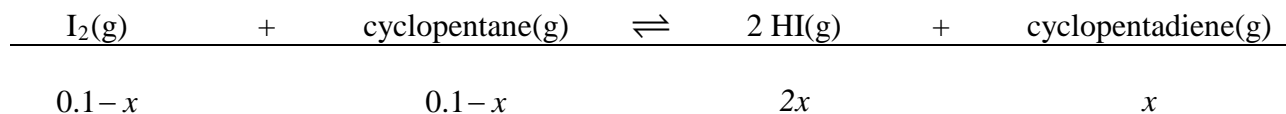
$$\Delta G^\circ = -17 \text{ 964.488 26 J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -18.0 \text{ kJ mol}^{-1}}$$

c. To calculate the equilibrium concentrations, we need to obtain the expression for the equilibrium constant  $K_c$ .

$$K_c = \frac{[\text{HI}]^2 [\text{cyclopentadiene}]}{[\text{I}_2][\text{cyclopentane}]}$$

At equilibrium, we have



Therefore  $K_c$  becomes,

$$K_c = \frac{(2x)^2 x}{(0.1-x)(0.1-x)}$$

$$K_c = \frac{4x^3}{(0.1-x)^2}$$

Solving for  $x$ , we can obtain the equilibrium concentrations.

$$0.040\,368\,\text{dm}^3\,\text{mol}^{-1} = \frac{4x^3}{(0.1-x)^2}$$

$$0.040\,368\,\text{dm}^3\,\text{mol}^{-1} (0.1-x)^2 = 4x^3$$

$$0.040\,368\,\text{dm}^3\,\text{mol}^{-1} (0.01 - 0.2x + x^2) = 4x^3$$

$$4.0368 \times 10^{-4}\,\text{dm}^3\,\text{mol}^{-1} - (8.0736 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1})x + (4.0368 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1})x^2 - 4x^3 = 0$$

To obtain  $x$  we can graph the equation and find the solution.

$$x = 0.005\,006\,32\,\text{mol}\,\text{dm}^{-3}$$

$$[\text{cyclopentadiene}] = x = 0.005\,006\,32 \text{ mol dm}^{-3}$$

$$[\text{cyclopentadiene}] = 5.01 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{HI}] = 2x = 2(0.005\,006\,32 \text{ mol dm}^{-3})$$

$$[\text{HI}] = 0.010\,012\,64 \text{ mol dm}^{-3}$$

$$[\text{HI}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{I}_2] = [\text{cyclopentane}] = 0.1 - x$$

$$[\text{I}_2] = [\text{cyclopentane}] = 0.09499368 \text{ mol dm}^{-3}$$

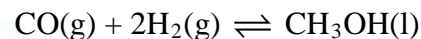
$$[\text{I}_2] = [\text{cyclopentane}] = 9.50 \times 10^{-2} \text{ mol dm}^{-3}$$

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**4.35.** From the data in Appendix D, for the synthesis of methanol,



Calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  and the equilibrium constant at 25 °C.

**Solution:**

Given: Appendix D,  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$ ,  $K$

From Eq. 2.53 the enthalpies of formation can be used to obtain  $\Delta H^\circ$  for each reaction.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = (-239.2 \text{ kJ mol}^{-1}) - (-110.53 \text{ kJ mol}^{-1} + 2(0))$$

$$\Delta H^\circ = -128.67 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H^\circ = -128.7 \text{ kJ mol}^{-1}}$$

From Eq. 3.91 the Gibbs energies of formation can be used to obtain  $\Delta G^\circ$  for each reaction.

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = (-166.6 \text{ kJ mol}^{-1}) - (\text{kJ mol}^{-1} + 2(0))$$

$$\Delta G^\circ = - \text{kJ mol}^{-1}$$

$$\boxed{\Delta G^\circ = \text{kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{- \text{J mol}^{-1} - (- \text{J mol}^{-1})}{298.15 \text{ K}}$$

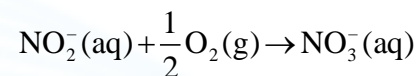
$$\Delta S^\circ = - \text{J mol}^{-1} \text{ K}$$

$$\boxed{\Delta S^\circ = - \text{J mol}^{-1} \text{ K}}$$

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- 4.36.** The bacterium *nitrobacter* plays an important role in the “nitrogen cycle” by oxidizing nitrite to nitrate. It obtains the energy it requires for growth from the reaction



Calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  for this reaction from the following data, at 25 °C:

Ion	$\frac{\Delta_f H^\circ}{\text{kJ mol}^{-1}}$	$\frac{\Delta_f G^\circ}{\text{kJ mol}^{-1}}$
$\text{NO}_2^-$	-104.6	-37.2
$\text{NO}_3^-$	-207.4	-111.3

**Solution:**

Given:  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$

From Eq. 2.53 the enthalpies of formation can be used to obtain  $\Delta H^\circ$  for each reaction.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = (-207.4 \text{ kJ mol}^{-1}) - \left( -104.6 \text{ kJ mol}^{-1} + \frac{1}{2}(0) \right)$$

$$\boxed{\Delta H^\circ = -102.8 \text{ kJ mol}^{-1}}$$

From Eq. 3.91 the Gibbs energies of formation can be used to obtain  $\Delta G^\circ$  for each reaction.

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = (-111.3 \text{ kJ mol}^{-1}) - \left( -37.2 \text{ kJ mol}^{-1} + \frac{1}{2}(0) \right)$$

$$\boxed{\Delta G^\circ = -74.1 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{-102.8 \times 10^3 \text{ J mol}^{-1} - (-74.1 \times 10^3 \text{ J mol}^{-1})}{298.15 \text{ K}}$$

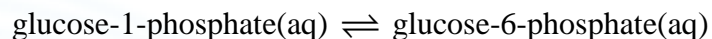
$$\Delta S^\circ = -96.260 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\boxed{\Delta S^\circ = -96.26 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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4.37. When the reaction:



is at equilibrium at 25 °C, the amount of glucose-6-phosphate present is 95% of the total.

a. Calculate  $\Delta G^\circ$  at 25 °C.

b. Calculate  $\Delta G$  for reaction in the presence of  $10^{-2}$  M glucose-1-phosphate and  $10^{-4}$  M glucose-6-phosphate. In which direction does reaction occur under these conditions?

**Solution:**

Given:  $T = 25^\circ\text{C} = 298.15\text{ K}$ ,  $x_{\text{glucose-6-phosphate}} = 0.95$

Required:

a. To calculate  $\Delta G^\circ$ , we first find the equilibrium constant for the reaction.

$$K = \frac{[\text{glucose-6-phosphate}]}{[\text{glucose-1-phosphate}]}$$

$$K = \frac{x_{\text{glucose-6-phosphate}}}{1 - x_{\text{glucose-6-phosphate}}}$$

solving for  $K$  gives,

$$K = \frac{0.95}{1 - 0.95}$$

$$K = 19$$

The relationship between  $K$  and  $\Delta G^\circ$  is given by,  $\Delta G^\circ = -RT \ln K$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1}\right)(298.15 \text{ } \cancel{\text{K}})\ln(19)$$

$$\Delta G^\circ = -7299.170 \text{ 52 J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -7.3 \text{ kJ mol}^{-1}}$$

b. To calculate  $\Delta G$ , we follow the same procedure as part a, and first find the equilibrium constant for the reaction. The  $\Delta G$  will be the difference in standard Gibbs energy,  $\Delta G^\circ$  and the Gibbs energy for  $K=10^{-2}$ .

$$K = \frac{[\text{glucose} - 6 - \text{phosphate}]}{[\text{glucose} - 1 - \text{phosphate}]} = \frac{10^{-4}}{10^{-2}} = 10^{-2}$$

Solving for  $\Delta G$  gives,

$$\Delta G_{K=10^{-2}} = -\left(8.3145 \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1}\right)(298.15 \text{ } \cancel{\text{K}})\ln(10^{-2})$$

$$\Delta G_{K=10^{-2}} = 11\,416.070 \text{ 33 J mol}^{-1}$$

$$\Delta G = \Delta G^\circ - \Delta G_{K=10^{-2}}$$

$$\Delta G = -7299.170 \text{ 52 J mol}^{-1} - 11\,416.070 \text{ 33 J mol}^{-1}$$

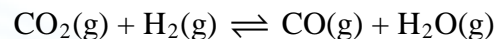
$$\Delta G = -18\,715.245 \text{ 35 J mol}^{-1}$$

$$\boxed{\Delta G = -19 \text{ kJ mol}^{-1}}$$

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**4.38.** From the data in Appendix D, for the reaction



Calculate the following:

- $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  (standard state: 1 bar and 25 °C).
- The equilibrium constant at 25 °C.
- From the heat capacity data in Table 2.1, obtain an expression for  $\Delta H^\circ$  as a function of temperature.
- Obtain an expression for  $\ln K_P$  as a function of temperature.
- Calculate  $K_P$  at 1000 K.

**Solution:**

Given: Appendix D,  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:

- From Eq. 2.53 the enthalpies of formation can be used to obtain  $\Delta H^\circ$  for each reaction.

$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta H^\circ = (-110.53 \text{ kJ mol}^{-1} + -241.826 \text{ kJ mol}^{-1}) - (-393.51 \text{ kJ mol}^{-1} + (0))$$

$$\boxed{\Delta H^\circ = 41.154 \text{ kJ mol}^{-1}}$$

From Eq. 3.91 the Gibbs energies of formation can be used to obtain  $\Delta G^\circ$  for each reaction.

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta G^\circ = (-111.3 \text{ kJ mol}^{-1}) - (\text{kJ mol}^{-1} + -228.6 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta G^\circ = \text{kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{-102.8 \times 10^3 \text{ J mol}^{-1} - (-74.1 \times 10^3 \text{ J mol}^{-1})}{298.15 \text{ K}}$$

$$\Delta S^\circ = -96.26027 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\boxed{\Delta S^\circ = -96.26 \text{ J K}^{-1} \text{ mol}^{-1}}$$

b. The relationship between  $K$  and...

c. Heat capacity is given by equation 2.52 as,

$$\Delta H_m(T_2) = \Delta H_m(T_1) + \Delta d(T_2) + \frac{1}{2} \Delta e(T_2^2 - T_1^2) - \Delta f \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

From the values in Table 2.1 we can obtain  $d$ ,  $e$  and  $f$ .

$$\Delta d = d(\text{products}) - d(\text{reactants})$$

$$\Delta d = (28.41 + 30.54) - (44.22 + 27.28)$$

$$\Delta d = -12.55 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta e = e(\text{products}) - e(\text{reactants})$$

$$\Delta e = (4.10 + 10.29) \times 10^{-3} - (8.79 + 3.26) \times 10^{-3}$$

$$\Delta e = 2.34 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$$



$$\Delta f = f(\text{products}) - f(\text{reactants})$$

$$\Delta f = (-4.6 + 0) \times 10^4 - (-86.2 + 5.0) \times 10^4$$

$$\Delta f = 76.6 \times 10^4 \text{ J K mol}^{-1}$$

Solving for an expression for  $\Delta H^\circ$  as a function of temperature gives,

$$\begin{aligned} \Delta H^\circ(T_2) &= 41\,154 \text{ J mol}^{-1} - 12.55 \text{ J K}^{-1} \text{ mol}^{-1}(T_2) + \frac{1}{2}(2.34 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1})(T_2^2 - (298.15 \text{ K})^2) \\ &\quad - 76.6 \times 10^4 \text{ J K mol}^{-1} \left( \frac{1}{T_2} - \frac{1}{298.15 \text{ K}} \right) \end{aligned}$$

Simplifying we obtain,

$$\Delta H^\circ(T_2) = 41\,154 - 12.55T_2 + (1.17 \times 10^{-3})(T_2^2 - (298.15)^2) - 76.6 \times 10^4 \left( \frac{1}{T_2} - \frac{1}{298.15} \right)$$

$$\Delta H^\circ(T_2) = 41\,154 - 12.55T_2 + 1.17 \times 10^{-3}T_2^2 - (1.17 \times 10^{-3})(298.15)^2 - \frac{76.6 \times 10^4}{T_2} + \frac{76.6 \times 10^4}{298.15}$$

$$\Delta H^\circ(T_2) = 41\,154 - 12.55T_2 + 1.17 \times 10^{-3}T_2^2 - 104.005 - \frac{76.6 \times 10^4}{T_2} + 2569.177$$

$$\Delta H^\circ(T_2) = 43\,619.172 - 12.55T_2 + 1.17 \times 10^{-3}T_2^2 - \frac{76.6 \times 10^4}{T_2}$$

$\Delta H^\circ(T) = 43\,619 \text{ J mol}^{-1} + 1.17 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}T^2 - 12.55 \text{ J K}^{-1} \text{ mol}^{-1}T - \frac{76.6 \times 10^4 \text{ J K mol}^{-1}}{T}$
--

d. To obtain an expression for  $\ln K_P$ , we use Eq. 4.72,

$$\frac{d \ln K_P^\circ}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Rearranging for  $\ln K_P$  gives,

$$d \ln K_p = \frac{\Delta H^\circ}{RT^2} dT$$

$$\ln K_p = \int \frac{\Delta H^\circ}{RT^2} dT$$

Substituting the expression obtained in part c., we obtain,

$$\Delta H^\circ(T) = 43\,619 + 1.17 \times 10^{-3} T^2 - 12.55 T - \frac{76.6 \times 10^4}{T}$$

$$\ln K_p = \int \frac{\Delta H^\circ}{RT^2} dT$$

$$\ln K_p = \int \frac{43\,619}{RT^2} + \frac{1.17 \times 10^{-3} T^2}{R T^2} - \frac{12.55 T}{R T^2} - \frac{76.6 \times 10^4}{R T^3} \frac{1}{T} dT$$

$$\ln K_p = \int \frac{43\,619}{RT^2} + \frac{1.17 \times 10^{-3}}{R} - \frac{12.55}{RT} - \frac{76.6 \times 10^4}{RT^3} dT$$

$$\ln K_p = \frac{1}{R} \int 1.17 \times 10^{-3} - \frac{12.55}{T} + \frac{43\,619}{T^2} - \frac{76.6 \times 10^4}{T^3} dT$$

$$\ln K_p = \frac{1}{R} \left[ 1.17 \times 10^{-3} T - 12.55 \ln T - \frac{43\,619}{T} + \frac{76.6 \times 10^4}{2T^2} \right] + I, \text{ where } I \text{ is an integration factor}$$

$$\ln K_p = \frac{1}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left[ 1.17 \times 10^{-3} \cancel{\text{K}} (1000 \text{ K}) - 12.55 \ln(1000 \text{ K}) - \frac{43\,619}{(1000 \text{ K})} + \frac{38.3 \times 10^4}{(1000 \cancel{\text{K}})^2} \right]$$

$$\ln K_p = \frac{1}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left[ 1.17 \times 10^{-3} \cancel{\text{K}} (1000 \text{ K}) - 12.55 \ln(1000 \text{ K}) - \frac{43\,619}{(1000 \text{ K})} + \frac{38.3 \times 10^4}{(1000 \cancel{\text{K}})^2} \right]$$

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To obtain  $I$ , we use the result from part b.

$$\ln K_p = \frac{1}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left[ \frac{1.17 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1}}{T} - \frac{43\,619 \text{ J mol}^{-1}}{T} + \right]$$

e. To calculate  $K_p$  at 1000 K, we use the expression obtained in part d.

**4.39.** Irving Langmuir [*J. Amer. Chem. Soc.*, 28, 1357 (1906)] studied the dissociation of  $\text{CO}_2$  into CO and  $\text{O}_2$  by bringing the gas at 1 atm pressure into contact with a heated platinum wire. He obtained the following results:

$T/\text{K}$	Percent Dissociation
1395	0.0140
1443	0.0250
1498	0.0471

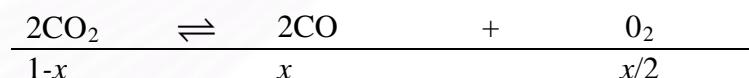
Calculate  $K_P$  for  $2\text{CO}_2(\text{g}) = 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$  at each temperature, and estimate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  at 1395 K.

**Solution:**

Given:  $P = 1\text{atm}$ , percent dissociation

Required:  $K_P$  at  $T=1395$ ,  $K_P$  at  $T=1443$ ,  $K_P$  at  $T=1498$ ,  $\Delta H^\circ_{T=1395}$ ,  $\Delta G^\circ_{T=1395}$ ,  $\Delta S^\circ_{T=1395}$

To determine  $K_P$  we find an expression in terms of the amounts of  $\text{CO}_2$ , CO and  $\text{O}_2$ .



$$K_P = \frac{(x_{\text{CO}})^2 x_{\text{O}_2}}{(x_{\text{CO}_2})^2}$$

$$K_P = \frac{(x)^2 \left(\frac{x}{2}\right)}{(1-x)^2}$$

$$K_P = \frac{1}{2} \frac{x^3}{(1-x)^2}$$

Solving for  $K_P$  at each temperature gives,

$$K_{P \text{ at } T=1395} = \frac{1}{2} \frac{(0.0140 \times 10^{-2})^3}{(1 - 0.0140 \times 10^{-2})^2}$$

$$K_{P \text{ at } T=1395} = 1.372 \ 38 \times 10^{-12} \text{ atm}$$

where 1 atm = 1.01325 bar

$$K_{P \text{ at } T=1395} = 1.390 \ 57 \times 10^{-12} \text{ bar}$$

$$\boxed{K_{P \text{ at } T=1395} = 1.39 \times 10^{-12} \text{ bar}}$$

$$K_{P \text{ at } T=1443} = \frac{1}{2} \frac{(0.0250 \times 10^{-2})^3}{(1 - 0.0250 \times 10^{-2})^2}$$

$$K_{P \text{ at } T=1443} = 7.816 \ 41 \times 10^{-12} \text{ atm}$$

where 1 atm = 1.01325 bar

$$K_{P \text{ at } T=1443} = 7.919 \ 98 \times 10^{-12} \text{ bar}$$

$$\boxed{K_{P \text{ at } T=1443} = 1.39 \times 10^{-12} \text{ bar}}$$

$$K_{P \text{ at } T=1498} = \frac{1}{2} \frac{(0.0471 \times 10^{-2})^3}{(1 - 0.0471 \times 10^{-2})^2}$$

$$K_{P \text{ at } T=1498} = 5.229 \ 28 \times 10^{-11} \text{ atm}$$

where 1 atm = 1.01325 bar

$$K_{P \text{ at } T=1498} = 5.298 \ 57 \times 10^{-11} \text{ bar}$$

$$\boxed{K_{P \text{ at } T=1498} = 5.30 \times 10^{-11} \text{ bar}}$$

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- 4.40.** G. Stark and M. Bodenstein [*Z. Electrochem.*, 16, 961(1910)] carried out experiments in which they sealed iodine in a glass bulb and measured the vapor pressure. The following are some of the results they obtained:

volume of bulb = 249.8 cm<sup>3</sup>

amount of iodine = 1.958 mmol

Temperature/°C	Pressure/Torr
800	558.0
1000	748.0
1200	1019.2

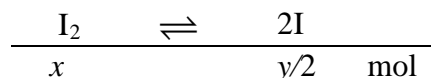
- Calculate the degree of dissociation at each temperature.
- Calculate  $K_c$  at each temperature, for the process  $\text{I}_2 \rightleftharpoons 2\text{I}$ .
- Calculate  $K_p$  at each temperature.
- Obtain values for  $\Delta H^\circ$  and  $\Delta U^\circ$  at 1000 °C.
- Calculate  $\Delta G^\circ$  and  $\Delta S^\circ$  at 1000 °C.

**Solution:**

Given:  $n = 1.958 \times 10^{-3}$  mol,  $V = 249.8 \times 10^{-3}$  dm<sup>3</sup>

Required:

- a. The reaction in this problem is given by



The degree of dissociation,  $\alpha$ , can be obtained by first determining the number of moles of  $\text{I}_2$  and  $\text{I}$  present.

The total number of moles present at equilibrium is given by,

$$x + \frac{y}{2} = 1.958 \times 10^{-3} \text{ mol} \quad (1)$$

To obtain a second expression involving  $x$  and  $y$ , we rearrange the ideal gas law, and solve for  $x$  and  $y$ .

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$x + y = \frac{PV}{RT}$$

$$x + y = \frac{\left( 558.0 \cancel{\text{ torr}} \times \frac{1 \cancel{\text{ atm}}}{760.0 \cancel{\text{ torr}}} \right) (249.8 \times 10^{-3} \cancel{\text{ dm}^3})}{(0.08206 \cancel{\text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}}) (1073.15 \cancel{\text{ K}})}$$

$$x + y = 2.08267 \times 10^{-3} \text{ mol} \quad (2)$$

Now we have two equations and two unknowns, and subtracting (1) from (2), we can obtain  $y$ .

$$\frac{y}{2} = 1.2467 \times 10^{-4} \text{ mol}$$

$$y = 2.4934 \times 10^{-4} \text{ mol}$$

$$x = 2.08267 \times 10^{-3} \text{ mol} - 2.4934 \times 10^{-4} \text{ mol}$$

$$x = 1.8333 \times 10^{-3} \text{ mol}$$

Solving for the degree of dissociation,

$$\alpha_{T=1073.15\text{ K}} = 1 - \frac{x}{n_{\text{total}}} = 1 - \frac{x}{\left(x + \frac{y}{2}\right)}$$

$$\alpha_{T=1073.15\text{ K}} = 1 - \frac{1.8333 \times 10^{-3} \text{ mol}}{1.958 \times 10^{-3} \text{ mol}}$$

$$\alpha_{T=1073.15\text{ K}} = 0.063\,874$$

$$\boxed{\alpha_{T=1073.15\text{ K}} = 6.39 \times 10^{-2}}$$

Repeating this procedure, we can determine  $\alpha$  at 1273.15 K,

$$x + y = \frac{PV}{RT}$$

$$x + y = \frac{\left(748.0 \cancel{\text{ torr}} \times \frac{1 \cancel{\text{ atm}}}{760.0 \cancel{\text{ torr}}}\right) (249.8 \times 10^{-3} \cancel{\text{ dm}^3})}{(0.082\,06 \cancel{\text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}}) (1273.15 \cancel{\text{ K}})}$$

$$x + y = 2.353\,25 \times 10^{-3} \text{ mol} \quad (3)$$

Now we have two equations and two unknowns, and subtracting (1) from (3), we can obtain  $y$ .

$$\frac{y}{2} = 3.9525 \times 10^{-4} \text{ mol}$$

$$y = 7.905 \times 10^{-4} \text{ mol}$$

$$x = 2.353\,25 \times 10^{-3} \text{ mol} - 7.905 \times 10^{-4} \text{ mol}$$

$$x = 1.562\,75 \times 10^{-3} \text{ mol}$$

Solving for the degree of dissociation,

$$\alpha_{T=1273.15\text{ K}} = 1 - \frac{x}{n_{\text{total}}} = 1 - \frac{x}{\left(x + \frac{y}{2}\right)}$$

$$\alpha_{T=1273.15\text{ K}} = 1 - \frac{1.562\,75 \times 10^{-3}\text{ mol}}{1.958 \times 10^{-3}\text{ mol}}$$

$$\alpha_{T=1273.15\text{ K}} = 0.201\,86$$

$$\boxed{\alpha_{T=1273.15\text{ K}} = 0.202}$$

Repeating this procedure, we can determine  $\alpha$  at 1473.15,

$$x + y = \frac{PV}{RT}$$

$$x + y = \frac{\left(1019.2 \cancel{\text{ torr}} \times \frac{1 \cancel{\text{ atm}}}{760.0 \cancel{\text{ torr}}}\right) (249.8 \times 10^{-3} \cancel{\text{ dm}^3})}{(0.082\,06 \cancel{\text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}}) (1473.15 \cancel{\text{ K}})}$$

$$x + y = 2.771\,15 \times 10^{-3}\text{ mol} \quad (4)$$

Now we have two equations and two unknowns, and subtracting (1) from (3), we can obtain  $y$ .

$$\frac{y}{2} = 8.1315 \times 10^{-4}\text{ mol}$$

$$y = 1.6263 \times 10^{-3}\text{ mol}$$

$$x = 2.771\,15 \times 10^{-3}\text{ mol} - 7.905 \times 10^{-4}\text{ mol}$$

$$x = 1.144\,85 \times 10^{-3}\text{ mol}$$

Solving for the degree of dissociation,



$$\alpha_{T=1473.15 \text{ K}} = 1 - \frac{x}{n_{\text{total}}} = 1 - \frac{x}{\left(x + \frac{y}{2}\right)}$$

$$\alpha_{T=1473.15 \text{ K}} = 1 - \frac{1.144\,85 \times 10^{-3} \text{ mol}}{1.958 \times 10^{-3} \text{ mol}}$$

$$\alpha_{T=1473.15 \text{ K}} = 0.415\,30$$

$$\boxed{\alpha_{T=1473.15 \text{ K}} = 0.415}$$

b. To determine the value of  $K_c$  at each temperature, we use the number of moles of  $\text{I}_2$  and  $\text{I}$ , i.e. the values of  $x$  and  $y$  obtained in part a. The expression for the equilibrium constant is given by,

$$K_c = \frac{[\text{I}]^2}{[\text{I}_2]}, \text{ where } C = \frac{n}{V}$$

$$K_c = \frac{\left(\frac{y}{V}\right)^2}{\left(\frac{x}{V}\right)}$$

$$K_c = \frac{y^2}{x} \frac{1}{V}$$

At  $T = 1073.15 \text{ K}$ ,

$$K_c = \frac{(2.4934 \times 10^{-4} \text{ mol})^2}{(1.8333 \times 10^{-3} \text{ mol})} \frac{1}{(249.8 \times 10^{-3} \text{ dm}^3)}$$

$$K_c = 1.357\,56 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\boxed{K_c = 1.358 \times 10^{-4} \text{ mol dm}^{-3}}$$

At  $T = 1273.15 \text{ K}$ ,

$$K_c = \frac{(7.905 \times 10^{-4} \text{ mol})^2}{(1.56275 \times 10^{-3} \text{ mol})(249.8 \times 10^{-3} \text{ dm}^3)}$$

$$K_c = 1.60074 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\boxed{K_c = 1.601 \times 10^{-3} \text{ mol dm}^{-3}}$$

At  $T = 1473.15 \text{ K}$ ,

$$K_c = \frac{(1.6263 \times 10^{-3} \text{ mol})^2}{(1.14485 \times 10^{-3} \text{ mol})(249.8 \times 10^{-3} \text{ dm}^3)}$$

$$K_c = 9.24827 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\boxed{K_c = 9.248 \times 10^{-3} \text{ mol dm}^{-3}}$$

c. The relationship between  $K_c$  and  $K_P$  is given by Eq. 4.26,

$K_P = K_c(RT)^{\Sigma \nu}$ , where  $\Sigma \nu$  is the difference between the moles of products to the moles of reactants.

Since there are two moles of I produced from one mole of  $\text{I}_2$ ,

$$\Sigma \nu = +1 \text{ mol}.$$

Solving for  $K_P$  at  $T = 1073.15 \text{ K}$  gives,

$$K_P = (1.35756 \times 10^{-4} \text{ mol dm}^{-3}) \left( (0.083145 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 1073.15 \text{ K})^{(+1)} \right)$$

$$K_P = 0.012113 \text{ bar}$$

$$\boxed{K_P = 0.0121 \text{ bar}}$$

At  $T = 1273.15 \text{ K}$ ,

$$K_p = \left(1.60\,074 \times 10^{-3} \cancel{\text{mol}} \cancel{\text{dm}^3}\right) \left(0.083\,145 \text{ bar} \cancel{\text{dm}^3} \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}} \times 1273.15 \text{ K}\right)^{(+1)}$$

$$K_p = 0.169\,448 \text{ bar}$$

$$\boxed{K_p = 0.1694 \text{ bar}}$$

At  $T = 1473.15 \text{ K}$ ,

$$K_p = \left(9.248\,27 \times 10^{-3} \cancel{\text{mol}} \cancel{\text{dm}^3}\right) \left(0.083\,145 \text{ bar} \cancel{\text{dm}^3} \cancel{\text{K}^{-1}} \cancel{\text{mol}^{-1}} \times 1473.15 \text{ K}\right)^{(+1)}$$

$$K_p = 1.132\,77 \text{ bar}$$

$$\boxed{K_p = 1.133 \text{ bar}}$$

d.

e. The relationship between  $K_p$  and  $\Delta G^\circ$  is given by Eq. 4.20,  $\Delta G^\circ = -RT \ln K_p^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J} \cancel{\text{K}^{-1}} \text{ mol}^{-1}\right) \left(1273.15 \text{ K}\right) \ln(0.169\,448 \text{ bar})$$

$$\Delta G^\circ = 18\,791.664 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 18.79 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{\text{J mol}^{-1} - (18\,791.664 \text{ J mol}^{-1})}{1273.15 \text{ K}}$$

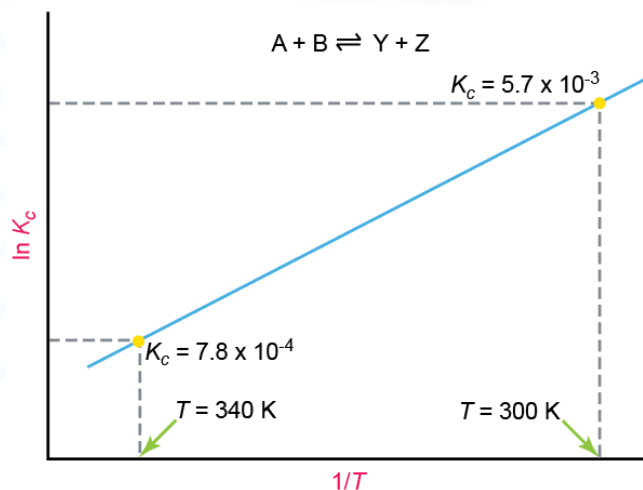
$$\Delta S^\circ = \text{J mol}^{-1} \text{ K}$$

$$\boxed{\Delta S^\circ = \text{J mol}^{-1} \text{ K}}$$

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- 4.41.** The following diagram shows the variation with temperature of the equilibrium constant  $K_c$  for a reaction. Calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 300 K.



**Solution:**

Given: Graph

Required:  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 300 K

The relationship between  $K_c$  and  $\Delta G^\circ$  is given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln(5.7 \times 10^{-3})$$

$$\Delta G^\circ = 12\,889.028 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 12.9 \text{ kJ mol}^{-1}}$$

The temperature dependence of equilibrium constants is given by Eq. 4.83 as

$$\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta U^\circ}{R}.$$

This can be written as,  $\frac{d \ln K_c^\circ}{d(1/T)} = -\frac{\Delta H^\circ}{R}$  since  $\Delta U^\circ$  and  $\Delta H^\circ$  are very close in solution.

Rearranging and solving for  $\Delta H^\circ$  gives,

$$\Delta H^\circ = -R \left( \frac{d \ln K_c^\circ}{d(1/T)} \right)$$

$$\Delta H^\circ = -R \left( \ln \left( \frac{K_{c2}}{K_{c1}} \right) \div \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1} \right) \left( \ln \left( \frac{5.7 \times 10^{-3}}{7.8 \times 10^{-4}} \right) \div \left( \frac{1}{300 \cancel{\text{K}}} - \frac{1}{340 \cancel{\text{K}}} \right) \right)$$

$$\Delta H^\circ = - \left( 8.3145 \text{ J mol}^{-1} \right) \left( \ln \left( \frac{5.7 \times 10^{-3}}{7.8 \times 10^{-4}} \right) \div (3.92157 \times 10^{-4}) \right)$$

$$\Delta H^\circ = -42\,169.192 \text{ J mol}^{-1}$$

$$\boxed{\Delta H^\circ = -42.2 \text{ kJ mol}^{-1}}$$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging and solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{-42\,169.192 \text{ J mol}^{-1} - (-12\,889.028 \text{ J mol}^{-1})}{300 \text{ K}}$$

$$\Delta S^\circ = -183.5274 \text{ J mol}^{-1} \text{ K}$$

$$\boxed{\Delta S^\circ = -184 \text{ J mol}^{-1} \text{ K}}$$

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**4.42.** The following values apply to a chemical reaction  $A \rightleftharpoons Z$ :

$$\Delta H^\circ = -85.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -170.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

Assuming these values to be temperature independent, calculate the equilibrium constant for the reaction at 300 K. At what temperature is the equilibrium constant equal to unity?

**Solution:**

Given:  $\Delta H^\circ = -85.2 \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = -170.2 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 300 \text{ K}$

Required:  $K_c$ ,  $T$  where  $K = 1$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -85.2 \times 10^3 \text{ J mol}^{-1} - (300 \text{ K})(-170.2 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G^\circ = -34140 \text{ J mol}^{-1}$$

The relationship between  $K_c$  and  $\Delta G^\circ$  is given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c$ . Rearranging and solving for  $K_c$  gives,

$$\ln K_c = \frac{-\Delta G^\circ}{RT}$$

$$K_c = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_c = e^{\frac{-(-34140 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}}$$

$$K_c = 879344.8912$$

$$\boxed{K_c = 8.79 \times 10^5}$$



The equilibrium constant is equal to unity when  $\Delta G^\circ$  is equal to zero.

$$\Delta G^\circ = -RT \ln(1)$$

$$\Delta G^\circ = -RT(0)$$

$$\Delta G^\circ = 0$$

Rearranging Eq. 3.90 we can obtain the temperature at which this occurs.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ - \Delta G^\circ}{\Delta S^\circ}, \text{ where } \Delta G^\circ = 0$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{-85.2 \times 10^3 \cancel{\text{ J mol}^{-1}}}{-170.2 \cancel{\text{ J K}^{-1} \text{ mol}^{-1}}}$$

$$T = 500.587 \text{ 54 K}$$

$$\boxed{T = 501 \text{ K}}$$

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**4.43.** The equilibrium constant  $K_c$  for the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and phosphate is  $1.66 \times 10^5 \text{ mol dm}^{-3}$  at  $37^\circ\text{C}$ , and  $\Delta H^\circ$  is  $-20.1 \text{ kJ mol}^{-1}$ . Calculate  $\Delta S^\circ$  for the hydrolysis at  $37^\circ\text{C}$ . On the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, calculate  $K_c$  at  $25^\circ\text{C}$ .

**Solution:**

Given:  $K_c = 1.66 \times 10^5 \text{ mol dm}^{-3}$ ,  $\Delta H^\circ = -20.1 \text{ kJ mol}^{-1}$   $T = 37^\circ\text{C} = 303.15 \text{ K}$

Required:  $\Delta S^\circ$  where  $T = 37^\circ\text{C} = 303.15 \text{ K}$ ,  $K_c$  where  $T = 25^\circ\text{C} = 298.15 \text{ K}$

The equilibrium in this problem is given by



The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

To obtain  $\Delta G^\circ$ , we use the relationship between  $K_c$  and  $\Delta G^\circ$ , given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(310.15 \text{ K}\right) \ln \left(1.66 \times 10^5 \text{ mol}^{-1} \text{ dm}^3\right)$$

$$\Delta G^\circ = -30\,995.818\,38 \text{ J mol}^{-1}$$

Solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{-20.1 \times 10^3 \text{ J mol}^{-1} - (-30\,995.818\,38 \text{ J mol}^{-1})}{303.15 \text{ K}}$$

$$\Delta S^\circ = 35.130\,802 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ = 35.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, we can calculate  $K_c$  from Eq. 4.27 by first obtaining  $\Delta G^\circ$  from Eq. 3.90 at 25 °C

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -20.1 \times 10^3 \text{ J mol}^{-1} - (298.15 \text{ K})(35.130 802 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G^\circ = -30 574.248 62 \text{ J mol}^{-1}$$

$$\Delta G^\circ = -RT \ln K_c^\circ$$

$$K_c = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K_c = e^{\frac{-(-30 574.248 62 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}}$$

$$K_c = 227 170.8135 \text{ mol dm}^{-3}$$

$$\boxed{K_c = 2.27 \times 10^5 \text{ mol dm}^{-3}}$$

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**4.44.** A dissociation  $A_2 \rightleftharpoons 2A$  has an equilibrium constant of  $7.2 \times 10^{-5} \text{ mol dm}^{-3}$  at 300 K, and a  $\Delta H^\circ$  value of  $40.0 \text{ kJ mol}^{-1}$ . Calculate the standard entropy change for the reaction at 300 K. (What is its standard state?) If the  $\Delta H^\circ$  and  $\Delta S^\circ$  values for this reaction are temperature independent, at what temperature is the equilibrium constant equal to unity?

**Solution:**

Given:  $K_c = 7.2 \times 10^{-5} \text{ mol dm}^{-3}$   $T = 300 \text{ K}$ ,  $\Delta H^\circ = 40.0 \text{ kJ mol}^{-1}$

Required:  $\Delta S^\circ$ ,  $T$  where  $K = 1$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

To obtain  $\Delta G^\circ$ , we use the relationship between  $K_c$  and  $\Delta G^\circ$ , given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(300 \text{ K}\right) \ln \left(7.2 \times 10^{-5} \text{ mol dm}^{-3}\right)$$

$$\Delta G^\circ = 23\,793.216\,63 \text{ J mol}^{-1}$$

Solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{40.0 \times 10^3 \text{ J mol}^{-1} - \left(23\,793.216\,63 \text{ J mol}^{-1}\right)}{300 \text{ K}}$$

$$\Delta S^\circ = 54.022\,611 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ = 54 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The equilibrium constant is equal to unity when  $\Delta G^\circ$  is equal to zero.

$$\Delta G^\circ = -RT \ln(1)$$

$$\Delta G^\circ = -RT(0)$$

$$\Delta G^\circ = 0$$

Rearranging Eq. 3.90 we can obtain the temperature at which this occurs.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ - \Delta G^\circ}{\Delta S^\circ}, \text{ where } \Delta G^\circ = 0$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{40.0 \times 10^3 \cancel{\text{ J mol}^{-1}}}{54.022 \, 611 \cancel{\text{ J K}^{-1} \text{ mol}^{-1}}}$$

$$T = 740.430 \, 706 \text{ K}$$

$$\boxed{T = 740 \text{ K}}$$

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**4.45.** A reaction  $A + B \rightleftharpoons Z$  has an equilibrium constant of  $4.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$  at 300 K, and a  $\Delta H^\circ$  value of  $-40.2 \text{ kJ mol}^{-1}$ . Calculate the entropy change for the reaction at 300 K. If the  $\Delta H^\circ$  and  $\Delta S^\circ$  values are temperature independent, at what temperature is the equilibrium constant equal to unity?

**Solution:**

Given:  $K_c = 4.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$   $T = 300 \text{ K}$ ,  $\Delta H^\circ = -40.2 \text{ kJ mol}^{-1}$

Required:  $\Delta S^\circ$ ,  $T$  where  $K = 1$

The relationship between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  is given by Eq. 3.90,

$$\Delta G = \Delta H - T\Delta S, \text{ hence, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Rearranging gives,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

To obtain  $\Delta G^\circ$ , we use the relationship between  $K_c$  and  $\Delta G^\circ$ , given by Eq. 4.27,  $\Delta G^\circ = -RT \ln K_c^\circ$

Solving for  $\Delta G^\circ$  gives,

$$\Delta G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(300 \text{ K}\right) \ln \left(4.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}\right)$$

$$\Delta G^\circ = -26\,725.507\,96 \text{ J mol}^{-1}$$

Solving for  $\Delta S^\circ$  gives,

$$\Delta S^\circ = \frac{-40.2 \times 10^3 \text{ J mol}^{-1} - \left(-26\,725.507\,96 \text{ J mol}^{-1}\right)}{300 \text{ K}}$$

$$\Delta S^\circ = -44.914\,973 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ = -44.9 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The equilibrium constant is equal to unity when  $\Delta G^\circ$  is equal to zero.

$$\Delta G^\circ = -RT \ln(1)$$

$$\Delta G^\circ = -RT(0)$$

$$\Delta G^\circ = 0$$

Rearranging Eq. 3.90 we can obtain the temperature at which this occurs.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ - \Delta G^\circ}{\Delta S^\circ}, \text{ where } \Delta G^\circ = 0$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{-40.2 \times 10^3 \cancel{\text{ J mol}^{-1}}}{-44.914\,973 \cancel{\text{ J K}^{-1} \text{ mol}^{-1}}}$$

$$T = 895.024\,472 \text{ K}$$

$$\boxed{T = 895 \text{ K}}$$

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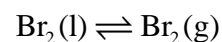
**4.46.** At 1 bar pressure liquid bromine boils at 58.2 °C, and at 9.3 °C its vapor pressure is 0.1334 bar. Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  to be temperature independent, calculate their values, and calculate the vapor pressure and  $\Delta G^\circ$  at 25 °C.

**Solution:**

Given:  $T_b = 58.2\text{ °C}$ ,  $P_{T=9.3\text{ °C}} = 0.1334\text{ bar}$ ,  $T = 25\text{ °C}$

Required:  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$

First of all, the equilibrium represented in this problem is given by



To solve for  $\Delta G^\circ$  we can use Eq. 4.20

$$\Delta G^\circ = -RT \ln K_p$$

We use the vapour pressure as a measure of the equilibrium constant and under the equilibrium conditions, ( $T_b = 58.2\text{ °C} = 331.35\text{ K}$ ) we obtain,

$$\Delta G^\circ(T = 331.35\text{ K}) = -(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(331.35\text{ K}) \ln(1\text{ bar})$$

$$\boxed{\Delta G^\circ(331.35\text{ K}) = 0\text{ J mol}^{-1}}$$

Where  $T = 9.3\text{ °C} = 282.45\text{ K}$ , we obtain

$$\Delta G^\circ(282.45\text{ K}) = -(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(282.45\text{ K}) \ln(0.1334\text{ bar})$$

$$\Delta G^\circ(282.45\text{ K}) = 4730.685837\text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ(282.45\text{ K}) = 4731\text{ J mol}^{-1}}$$

To solve for  $\Delta H^\circ$  and  $\Delta S^\circ$  we use Eq. 3.90,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . This method is applicable because the problem states that enthalpy and entropy are temperature independent.



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$4\,731\text{ J mol}^{-1} = \Delta H^\circ - (282.45\text{ K})\Delta S^\circ \quad (1)$$

$$0\text{ J mol}^{-1} = \Delta H^\circ - (331.35\text{ K})\Delta S^\circ \quad (2)$$

Subtracting (2) from (1) and then solving gives,

$$4\,730.685\,837\text{ J mol}^{-1} = (48.9\text{ K})\Delta S^\circ$$

$$\Delta S^\circ = \frac{4\,730.685\,837\text{ J mol}^{-1}}{48.9\text{ K}}$$

$$\Delta S^\circ = 96.742\,042\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\boxed{\Delta S^\circ = 96.74\text{ J K}^{-1}\text{ mol}^{-1}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$\Delta H^\circ = (331.35\text{ K})(96.742\,042\text{ J K}^{-1}\text{ mol}^{-1})$$

$$\Delta H^\circ = -32\,055.475\,5\text{ J mol}^{-1}$$

$$\boxed{\Delta H^\circ = 32\,055\text{ J mol}^{-1}}$$

To solve for the vapour pressure at  $T = 25^\circ\text{C} = 298.15\text{ K}$ , first we find the value for  $\Delta G^\circ$ , and solve for vapour pressure using Eq. 4.20.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 32\,055 \text{ J mol}^{-1} - (298.15 \text{ K})(96.74 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G^\circ = 3\,211.969 \text{ J mol}^{-1}$$

$$\Delta G^\circ = -RT \ln P$$

$$P = e^{\left(\frac{\Delta G^\circ}{RT}\right)}$$

$$P = e^{\left(\frac{3\,211.969 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}\right)}$$

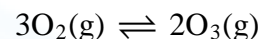
$$P = 0.273\,709\,522 \text{ bar}$$

$$\boxed{P = 0.273\,7 \text{ bar}}$$

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**4.47.** The standard Gibbs energy of formation of gaseous ozone at 25 °C,  $\Delta G_f^\circ$ , is 162.3 kJ mol<sup>-1</sup>, for a standard state of 1 bar. Calculate the equilibrium constants  $K_P$ ,  $K_c$ , and  $K_x$  for the process:



What is the mole fraction of O<sub>3</sub> present at 25 °C at 2 bar pressure?

**Solution:**

Given:  $T = 25\text{ °C} = 298.15\text{ K}$ ,  $\Delta G_f^\circ = 162.3\text{ kJ mol}^{-1}$ ,  $P = 2\text{ bar}$

Required:  $K_P$ ,  $K_c$ , and  $K_x$

First of all, the  $\Delta G^\circ$  for the reaction can be calculated from the standard Gibbs energy of formation for gaseous ozone as,

$$\Delta G^\circ = 2 \times \Delta G_f^\circ = 2 \times 162.3\text{ kJ mol}^{-1}$$

$$\Delta G^\circ = 324.6\text{ kJ mol}^{-1}$$

Rearranging Eq. 4.20, as shown in Problem 4.46, gives an expression for the  $K_P$

$$\Delta G^\circ = -RT \ln K_P$$

$$K_P = e^{\left(\frac{\Delta G^\circ}{RT}\right)}$$

$$K_P = e^{\left(\frac{324\,600\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1} \times 298.15\text{ K}}\right)}$$

$$K_P = 1.357\,68 \times 10^{-57}\text{ bar}^{-1}$$

$$\boxed{K_P = 1.36 \times 10^{-57}\text{ bar}^{-1}}$$

The unit of bar<sup>-1</sup> appears because the standard state is 1 bar.

The relationship between  $K_c$  and  $K_P$  is given by Eq. 4.26,

$K_P = K_c(RT)^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of products. Rearranging for  $K_c$  gives,

$$K_c = K_P(RT)^{-\Sigma v}$$

Since there are two moles of ozone produced from three moles of oxygen,  $\Sigma v = -1$  mol.

Solving for  $K_c$  gives,

$$K_c = K_p (RT)^{-\Sigma v}$$

$$K_c = (1.357\,68 \times 10^{-57} \text{ bar}^{-1}) \left( 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \right)^{-(-1)}$$

$$K_c = 3.365\,63 \times 10^{-54} \text{ J mol}^{-1} \text{ bar}^{-1}$$

where  $1 \text{ bar} = 10^5 \text{ Pa}$

$$K_c = \frac{3.365\,63 \times 10^{-54} \text{ J mol}^{-1} \text{ bar}^{-1}}{10^{-5} \text{ Pa bar}^{-1}}$$

$$K_c = 3.365\,63 \times 10^{-59} \text{ J mol}^{-1} \text{ Pa}^{-1}$$

where  $1 \text{ J Pa}^{-1} = 1 \text{ m}^3$  and therefore  $10^3 \text{ J Pa}^{-1} = 1 \text{ dm}^3$

$$\boxed{K_c = 3.37 \times 10^{-56} \text{ dm}^3 \text{ mol}^{-1}}$$

The relationship between  $K_x$  and  $K_p$  is given by Eq. 4.32,

$K_p = K_x P^{\Sigma v}$ , where  $\Sigma v$  is the difference between the moles of products to the moles of reactants.

Rearranging for  $K_x$  gives,

$$K_x = K_p P^{-\Sigma v}$$

Since there are two moles of ozone produced from three moles of oxygen,  $\Sigma v = -1$  mol.

Solving for  $K_x$  at  $P = 2 \text{ bar}$  gives,

$$K_x = K_p P^{-\Sigma v}$$

$$K_x = (1.357\,68 \times 10^{-57} \text{ bar}^{-1}) (2 \text{ bar}^{-1})^{-(-1)}$$

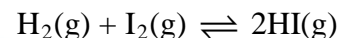
$$K_x = 2.715\,35 \times 10^{-57}$$

$$\boxed{K_x = 2.72 \times 10^{-57}}$$

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4.48. For the equilibrium:



The following data apply:

$$\Delta H^\circ(300\text{ K}) = -9.6\text{ kJ mol}^{-1}$$

$$\Delta S^\circ(300\text{ K}) = 22.18\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta C_p(500\text{ K}) = -7.11\text{ J K}^{-1}\text{ mol}^{-1}$$

The latter value can be taken to be the average value between 300 K and 500 K.

Calculate the equilibrium constants  $K_P$ ,  $K_c$ , and  $K_x$  at 500 K. What would be the mole fraction of HI present at equilibrium if HI is introduced into a vessel at 10 atm pressure; how would the mole fraction change with pressure?

**Solution:**

Given:  $\Delta H^\circ(300\text{ K}) = -9.6\text{ kJ mol}^{-1}$ ,  $\Delta S^\circ(300\text{ K}) = 22.18\text{ J K}^{-1}\text{ mol}^{-1}$ ,

$$\Delta C_p(500\text{ K}) = -7.11\text{ J K}^{-1}\text{ mol}^{-1}, P = 10\text{ atm}$$

Required:  $K_P$ ,  $K_c$ , and  $K_x$  at 500 K,  $x$

The relationship between enthalpy and heat capacity for changes in temperature is given by Eq. 2.46.

$$\Delta(\Delta H) = \Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$$

Therefore at  $T = 500\text{ K}$ , the enthalpy for the equilibrium becomes,

$$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$$

$$\Delta H_{500\text{ K}} = -9\,600\text{ J mol}^{-1} - 7.11\text{ J K}^{-1}\text{ mol}^{-1}(500\text{ K} - 300\text{ K})$$

$$\Delta H_{500\text{ K}} = -9\,600\text{ J mol}^{-1} - 7.11\text{ J K}^{-1}\text{ mol}^{-1}(200\text{ K})$$

$$\Delta H_{500\text{ K}} = -11\,022\text{ J mol}^{-1}$$

To determine the entropy change at  $T = 500$  K, we derive an equation for the temperature dependence of entropy and heat capacity from the relationship between entropy and enthalpy at equilibrium.

$$\text{at equilibrium, } \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

Using Eq. 2.46 and integrating we then obtain,

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$\Delta S^\circ(T_2) = \Delta S^\circ(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_p dT}{T}$$

$$\Delta S^\circ(T_2) = \Delta S^\circ(T_1) + \Delta C_p \ln \frac{T_2}{T_1}$$

$$\Delta S^\circ(T_{500 \text{ K}}) = 22.18 \text{ J K}^{-1} \text{ mol}^{-1} - 7.11 \text{ J K}^{-1} \text{ mol}^{-1} \ln \left( \frac{500 \text{ K}}{300 \text{ K}} \right)$$

$$\Delta S^\circ(T_{500 \text{ K}}) = 18.548 \, 029 \, 82 \text{ J K}^{-1} \text{ mol}^{-1}$$

The Gibbs free energy at  $T = 500$  K is,

$$\Delta G^\circ(500 \text{ K}) = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ(500 \text{ K}) = (-11 \, 022 \text{ J mol}^{-1}) - (500 \text{ K})(18.548 \, 029 \, 82 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G^\circ(500 \text{ K}) = -20 \, 296.014 \, 91 \text{ J mol}^{-1}$$

The relationship between Gibbs free energy and  $K_P$  is given by Eq. 4.20. Rearranging as shown in Problem 4.46, gives an expression for the  $K_P$

$$\Delta G^\circ = -RT \ln K_p$$

$$K_p = e^{\left(\frac{-\Delta G^\circ}{RT}\right)}$$

$$K_p = e^{\left(\frac{-20296.01491 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}\right)}$$

$$K_p = 131.9043544$$

$$\boxed{K_p = 132}$$

The relationship between  $K_c$  and  $K_p$  is given by Eq. 4.26,

$$K_p = K_c(RT)^{\Sigma \nu},$$

The relationship between  $K_x$  and  $K_p$  is given by Eq. 4.32,

$K_p = K_x P^{\Sigma \nu}$ , where  $\Sigma \nu$  is the difference between the moles of products to the moles of reactants. Since there is no change in the number of moles of products and reactants,  $K_c$  and  $K_x$  have the same value as  $K_p$  and therefore,

$$\boxed{K_p = K_c = K_x = 132}$$

To find the mole fraction, we determine the expression for  $K_x$  based on the equilibrium.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
$n_{\text{initial}}$	1		1		0
$n_{\text{equilibrium}}$	$-x$		$-x$		$+2x$
$n_{\text{final}}$	$1-x$		$1-x$		$2x$

$$K_x = \frac{(2x)^2}{(1-x)^2} = \frac{4x^2}{(1-x)^2}$$

solving for  $x$ , we obtain

$$\frac{4x^2}{(1-x)^2} = 132$$

$$\frac{2x}{1-x} = \sqrt{132}$$

$$2x = (11.489\,125\,29)(1-x)$$

$$x = \frac{11.489\,125\,29}{13.489\,125\,29}$$

$$x = 0.851\,732\,417$$

$$\boxed{x = 0.852}$$

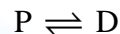
Pressure has no effect on the mole fraction.

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**\*4.49.** Protein denaturations are usually irreversible but may be reversible under a narrow range of conditions. At pH 2.0, at temperatures ranging from about 40 °C to 50 °C, there is an equilibrium between the active form P and the deactivated form D of the enzyme trypsin:



Thermodynamic values are  $\Delta H^\circ = 283 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 891 \text{ J K}^{-1} \text{ mol}^{-1}$ . Assume these values to be temperature independent over this narrow range, and calculate  $\Delta G^\circ$  and  $K_c$  values at 40.0 °C, 42.0 °C, 44.0 °C, 46.0 °C, 48.0 °C, and 50.0 °C. At what temperature will there be equal concentrations of P and D?

**\*\*Note** that the high thermodynamic values lead to a considerable change in  $K$  over this 10 °C range.

**Solution:**

Given: pH = 2.0,  $\Delta H^\circ = 283 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 891 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 40.0 \text{ °C}$ , 42.0 °C, 44.0 °C, 46.0 °C, 48.0 °C, and 50.0 °C

Required:  $\Delta G^\circ$  and  $K_c$  at  $T$  given,  $T_{\text{equilibrium}}$

To solve for  $\Delta G^\circ$  we use Eq. 3.90,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

For  $T = 40.0 \text{ °C}$ ,

$$\Delta G^\circ = 283\,000 \text{ J mol}^{-1} - (313.15 \text{ K})(891 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G^\circ = 3\,983.35 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 398 \text{ kJ mol}^{-1}}$$

The relationship between Gibbs free energy and  $K_c$  is given by Eq. 4.27. Rearranging gives an expression for the  $K_c$

$$\Delta G^\circ = -RT \ln K_c$$

$$K_c = e^{\left(\frac{\Delta G^\circ}{RT}\right)}$$

For  $T = 40.0 \text{ °C}$ ,

$$K_c = e^{\left( -\frac{3983.35 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 313.5 \text{ K}} \right)}$$

$$K_c = 0.21656$$

$$\boxed{K_c = 0.217}$$

Applying the same method to each temperature, we then obtain,

Temperature	$\Delta G^\circ \text{ kJ mol}^{-1}$	$K$
313.15	3.98	0.217
315.15	2.20	0.432
317.15	0.419	0.853
319.15	-1.362	1.67
321.15	-3.14	3.25
323.15	-4.93	6.26

The  $T_{\text{equilibrium}}$  occurs when

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$T_{\text{equilibrium}} = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T_{\text{equilibrium}} = \frac{283\,000 \cancel{\text{ J }} \cancel{\text{ mol}}^{-1}}{891 \cancel{\text{ J }} \text{ K}^{-1} \cancel{\text{ mol}}^{-1}}$$

$$T_{\text{equilibrium}} = 317.620\,651 \text{ K}$$

$$T_{\text{equilibrium}} = 317.6 \text{ K} = 44.47 \text{ }^\circ\text{C}$$

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**\*4.50.** Suppose that a large molecule, such as a protein, contains  $n$  sites to which a molecule A (a ligand) can become attached. Assume that the sites are equivalent and independent, so that the reactions  $M + A = MA$ ,  $MA + A = MA_2$ , etc., all have the same equilibrium constant  $K_s$ . Show that the average number of occupied sites per molecule is:

$$\bar{v} = \frac{nK_s[A]}{1 + K_s[A]}$$

**Solution:**

Given: above

Required: proof

If the concentration of M is  $[M]$ , then the total number of sites occupied and unoccupied is  $n[M]$ . The association of reactions may be formulated in terms of S, the number of sites.



The equilibrium constant becomes

$$K_s = \frac{[SA]}{[S][A]}, \text{ where } [S] \text{ is the concentration of unoccupied sites and } [SA] \text{ is the concentration of occupied sites.}$$

Rearranging the equilibrium constant in terms of  $[S]$  gives,

$$[S] = \frac{[SA]}{K_s[A]}$$

The total concentration of sites,  $n[M]$ , upon rearrangement, becomes,

$$n[M] = [S] + [SA]$$

$$n[M] = \frac{[SA]}{K_s[A]} + [SA]$$

$$n[M] = [SA] \left\{ \frac{1}{K_s[A]} + 1 \right\}$$

The average number of sites occupied per molecule is the total concentration of occupied sites divided by the total concentration of M.

$$\bar{v} = \frac{[SA]}{[M]} =$$

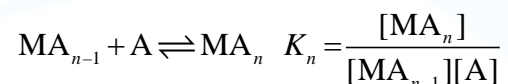
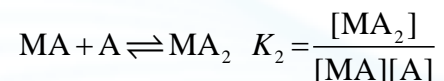
$$\bar{v} = \frac{n}{\frac{1}{K_s[A]} + 1}$$

$$\boxed{\bar{v} = \frac{nK_s[A]}{1 + K_s[A]}}$$

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**\*4.51.** Modify the derivation in Problem 4.50 so as to deal with sites that are not all equivalent; the equilibrium constants for the attachments of successive ligands are each different:



Show that the average number of molecules of A bound per molecule M is:

$$\bar{v} = \frac{K_1[A] + 2K_1K_2[A]^2 + \cdots + n(K_1K_2K_3 \cdots K_n)[A]^n}{1 + K_1[A] + K_1K_2[A]^2 + \cdots + (K_1K_2K_3 \cdots K_n)[A]^n}$$

This equation is important in biology and biochemistry and is often called the *Adair equation*, after the British biophysical chemist G. S. Adair.

**Solution:**

Given: above

Required: proof

The total concentration of the molecule M is

$$[M]_0 = [M] + [MA] + [MA_2] + \cdots + [MA_n]$$

The total concentration of the occupied sites is the total concentration of the bound A molecules,

$$[A]_b = [MA] + 2[MA_2] + \cdots + n[MA_n]$$

The first few equilibrium constants are given above as,

$$K_1 = \frac{[MA]}{[M][A]}, K_2 = \frac{[MA_2]}{[MA][A]}, K_3 = \frac{[MA_3]}{[MA_2][A]}$$

Rearranging the equilibrium constants in terms of [A] gives,

$$[MA] = K_1 [M][A]$$

$$[MA_2] = K_2 [MA][A] = K_1 K_2 [M][A]^2$$

$$[MA_3] = K_3 [MA_2][A] = K_1 K_2 K_3 [M][A]^3$$

Expressing every term in terms of [A] gives,

$$[A]_b = [MA] + 2[MA_2] + \dots + n[MA_n]$$

$$[A]_b = [M] \left\{ K_1 [A] + 2K_1 K_2 [A]^2 + \dots + n(K_1 K_2 \dots K_n) [A]^n \right\}$$

similarly,

$$[M]_0 = [M] + [MA] + [MA_2] + \dots + [MA_n]$$

$$[M]_0 = [M] \left\{ 1 + K_1 [A] + K_1 K_2 [A]^2 + \dots + (K_1 K_2 \dots K_n) [A]^n \right\}$$

The average number of molecules of A bound per molecule M is then given by

$$\bar{v} = \frac{[A]_b}{[M]_0}$$

$$\bar{v} = \frac{\cancel{[M]} \left\{ K_1 [A] + 2K_1 K_2 [A]^2 + \dots + n(K_1 K_2 \dots K_n) [A]^n \right\}}{\cancel{[M]} \left\{ 1 + K_1 [A] + K_1 K_2 [A]^2 + \dots + (K_1 K_2 \dots K_n) [A]^n \right\}}$$

$$\boxed{\bar{v} = \frac{K_1 [A] + 2K_1 K_2 [A]^2 + \dots + n(K_1 K_2 \dots K_n) [A]^n}{1 + K_1 [A] + K_1 K_2 [A]^2 + \dots + (K_1 K_2 \dots K_n) [A]^n}}$$

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**\*4.52.** Now show that the Adair equation, derived in Problem 4.51, reduces to the equation obtained in Problem 4.50 when the sites are equivalent and independent. [It is not correct simply to put  $K_1 = K_2 = K_3 \cdots = K_n$ ; certain statistical factors must be introduced. Thus, if  $K_s$  is the equilibrium constant for the binding at a given site,  $K_1 = nK_s$ , since there are  $n$  ways for  $A$  to become attached to a given molecule and one way for it to come off. Similarly  $K_2 = (n-1)K_s/2$ ;  $n-1$  ways on and 2 ways off. Continue this argument and develop an expression for  $\bar{v}$  that will factorize into  $nK_s[A]/(1 + K_s[A])$ . Suggest a method of testing the equilibrium obtained and arriving at a value of  $n$  from experimental data.]

**Solution:**

Given: Problems 4.50 and 4.51, information above

Required: prove that the Adair equation reduces to the equation in Problem 4.50

Using the above argument,

$$K_1 = nK_s$$

$$K_2 = (n-1) \frac{K_s}{2}$$

$$K_3 = (n-2) \frac{K_s}{3}$$

$$\text{and therefore, } K_n = \frac{K_s}{n}$$

Substituting this into the Adair equation we get,

$$\bar{v} = \frac{K_1[A] + 2K_1K_2[A]^2 + \dots + n(K_1K_2\dots K_n)[A]^n}{1 + K_1[A] + K_1K_2[A]^2 + \dots + (K_1K_2\dots K_n)[A]^n}$$

$$\bar{v} = \frac{nK_s[A] + n(n-1)K_s^2[A]^2 + \dots + nK_s^n[A]^n}{1 + nK_s[A] + n(n-1)K_s^2[A]^2 + \dots + K_s^n[A]^n}$$

The coefficients are the binomial coefficients and therefore the expression reduces to,



$$\bar{v} = \frac{nK_s [A] \left( 1 + (n-1)K_s [A] + \dots + K_s^{n-1} [A]^{n-1} \right)}{1 + nK_s [A] + n(n-1)K_s^2 [A]^2 + \dots + K_s^n [A]^n}$$

$$\bar{v} = \frac{nK_s [A] (1 + K_s [A])^{n-1}}{(1 + K_s [A])^n}$$

$$\bar{v} = \frac{nK_s [A] \cancel{(1 + K_s [A])^n}}{(1 + K_s [A]) \cancel{(1 + K_s [A])^n}}$$

$$\boxed{\bar{v} = \frac{nK_s [A]}{1 + K_s [A]}} \text{ which is the expression obtained in Problem 4.50.}$$

A method to test the equilibrium would be to plot  $\frac{1}{\bar{v}}$  against  $\frac{1}{[A]}$ . Rearranging the above equation gives,

$$\bar{v} = \frac{nK_s [A]}{1 + K_s [A]}$$

$$\frac{1}{\bar{v}} = \frac{1 + K_s [A]}{nK_s [A]}$$

$$\frac{1}{\bar{v}} = \frac{1}{nK_s [A]} + \frac{\cancel{K_s [A]}}{n \cancel{K_s [A]}}$$

$$\boxed{\frac{1}{\bar{v}} = \frac{1}{n} + \frac{1}{nK_s [A]}}$$

One of the intercepts will be  $\frac{1}{n}$ .

Alternatively,  $\bar{v}$  can be plotted against  $\frac{\bar{v}}{[A]}$

$$\bar{v} = \frac{nK_s[A]}{1 + K_s[A]}$$

$$\bar{v} + \bar{v}K_s[A] = nK_s[A]$$

$$\bar{v} = nK_s[A] - \bar{v}K_s[A]$$

$$\frac{\bar{v}}{K_s[A]} = n - \bar{v}$$

$$\boxed{\bar{v} = n - \frac{\bar{v}}{K_s[A]}}$$

[Back to Problem 4.52](#)

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**\*4.53.** Another special case of the equation derived in Problem 4.51 is if the binding on one site affects that on another. An extreme case is highly cooperative binding, in which the binding of A on one site influences the other sites so that they fill up immediately. This means that  $K_n$  is much greater than  $K_1, K_2$ , etc. Show that now:

$$\bar{v} = \frac{nK[A]^n}{1 + K[A]^n}$$

Where  $K$  is the product of  $K_1, K_2, \dots, K_n$ . The British physiologist A. V. Hill suggested that binding problems can be treated by plotting:

$$\ln \frac{\theta}{1-\theta} \quad \text{against} \quad \ln[A]$$

Where  $\theta$  is the fraction of sites that are occupied. Consider the significance of such *Hill plots*, especially their shapes and slopes, with reference to the equations obtained in Problems 4.50 to 4.53.

**Solution:**

Given: above

Required: proof

If  $K_n$  is much greater than  $K_1, K_2$ , and so on, then the equation obtained in Problem 4.51 reduces to the following

$$\bar{v} = \frac{K_1[A] + 2K_1K_2[A]^2 + \dots + n(K_1K_2\dots K_n)[A]^n}{1 + K_1[A] + K_1K_2[A]^2 + \dots + (K_1K_2\dots K_n)[A]^n}$$

$$\bar{v} = \frac{n(K_1K_2\dots K_n)[A]^n}{1 + (K_1K_2\dots K_n)[A]^n}$$

$$\boxed{\bar{v} = \frac{nK[A]^n}{1 + K[A]^n}}$$

Where  $K = K_1K_2\dots K_n$  is the overall equilibrium constant for the binding of  $n$  molecules, we then obtain



The fraction of sites occupied,  $\theta$

$$\theta = \frac{K[A]^n}{1 + K[A]^n} \text{ or, } \frac{\theta}{1 - \theta} = K[A]^n$$

The slope of the plot of  $\ln \frac{\theta}{1 - \theta}$  against  $[A]$  is therefore  $n$ . If the sites are identical and independent (Problem 4.50), then the slope is 1. Intermediate behaviour can give nonlinear plots; the maximum slope of a Hill plot cannot be greater than  $n$ .

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CHAPTER 5

Phases and Solutions

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Physical Chemistry

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Problems and Solutions

## Chapter 5

*\*problems with an asterisk are slightly more demanding*

### Thermodynamics of Vapor Pressure

- 5.1.** Diamonds have successfully been prepared by submitting graphite to high pressure. Calculate the approximate minimum pressure needed using  $\Delta_f G = 0$  for graphite and  $\Delta_f G = 2.90 \times 10^3 \text{ J mol}^{-1}$  for diamond. The densities of the two forms may be taken as independent of pressure and are  $2.25$  and  $3.51 \text{ g cm}^{-3}$ , respectively.
- [Solution](#)
- 5.2.** The molar entropy of vaporization of water is  $108.72 \text{ J K}^{-1}$  at  $760 \text{ Torr}$ . The corresponding densities of liquid water and water vapor are  $0.958 \text{ kg dm}^{-3}$  and  $5.98 \times 10^{-4} \text{ kg dm}^{-3}$ , respectively. Calculate the change of pressure for a one-degree change in temperature.
- [Solution](#)
- 5.3.** Calculate the heat of vaporization of water at  $373.15 \text{ K}$  and  $101.325 \text{ kPa}$  using the Clausius-Clapeyron equation. The vapor pressure of water is  $3.17 \text{ kPa}$  at  $298.15 \text{ K}$ . Compare your answer to the CRC Handbook<sup>1</sup> value.
- [Solution](#)
- 5.4.** Liquid water and vapor are in equilibrium at the triple point of water ( $0.00603 \text{ atm}$  and  $273.16 \text{ K}$ ). Assuming that the enthalpy of vaporization of water does not change over the temperature range considered, calculate the equilibrium vapor pressure of water at  $373.15 \text{ K}$ . Comment on the assumption made here. ( $\Delta_{\text{vap}} H^\circ = 40\,656 \text{ J mol}^{-1}$  at  $1 \text{ atm}$ .)
- [Solution](#)
- 5.5.** Estimate the vapor pressure of iodine under an external pressure of  $101.3 \times 10^6 \text{ Pa}$  at  $313.15 \text{ K}$ . The density of iodine is  $4.93 \text{ g cm}^{-3}$ . The vapor pressure at  $101.3 \text{ kPa}$  is  $133 \text{ Pa}$ .
- [Solution](#)
- 5.6.** The cubic expansion coefficient is given by  $\alpha = 1/V (\partial V / \partial T)_P$ . According to Ehrenfest's or Tisza's theory, find the order of the transition. Suggest what a plot of  $\alpha$  against  $T$  would look like near the transition point.
- [Solution](#)

<sup>1</sup>Handbook of Chemistry and Physics, 82nd ed., D. R. Lide, Ed., Boca Raton, FL: CRC Press, 2001.

- 5.7. The vapor pressure of *n*-propanol is 1.94 kPa at 293 K and 31.86 kPa at 343 K. What is the enthalpy of vaporization?

[Solution](#)

- 5.8. The compound 2-hydroxybiphenyl (*o*-phenylphenol) boils at 286 °C under 101.325 kPa and at 145 °C under a reduced pressure of 14 Torr. Calculate the value of the molar enthalpy of vaporization. Compare this value to that given in the CRC Handbook.

[Solution](#)

- 5.9. Using Trouton's rule, estimate the molar enthalpy of vaporization of *n*-hexane, the normal boiling point of which is 342.10 K. Compare the value obtained to the value 31.912 kJ mol<sup>-1</sup> obtained in vapor pressure studies.

[Solution](#)

- 5.10. The normal boiling point of toluene is 110.62 °C. Estimate its vapor pressure at 80.00 °C assuming that toluene obeys Trouton's rule.

[Solution](#)

- 5.11. 2-Propanone (acetone) boils at 329.35 K at 1 atm of pressure. Estimate its boiling point at 98.5 kPa using Crafts' rule.

[Solution](#)

- 5.12. The variation of the equilibrium vapor pressure with temperature for liquid and solid chlorine in the vicinity of the triple point is given by

$$\ln P_l = \frac{-2661}{T} + 22.76,$$

$$\ln P_s = \frac{-3755}{T} + 26.88.$$

Use *P*/pascal in the equations. Calculate the triple point pressure and temperature.

[Solution](#)

- 5.13. The boiling point of water at 102.7 kPa is 373.52 K. Calculate the value at 101.325 kPa (1 atm) using Crafts' rule.

[Solution](#)

- 5.14.** The vapor pressure of water at 27.5 °C, a calibration temperature for glassware used in warmer climates, is 27.536 Torr under its own vapor pressure. Calculate the vapor pressure of water under an air pressure of 1.00 atm. Assume that air is inert. The density of water at 27.5 °C is 996.374 g dm<sup>-3</sup>.

[Solution](#)

- 5.15.** Following the derivation of the expression for  $\Delta S$  in terms of  $\Delta G$  in Eq. 3.161, derive an expression for  $\Delta V$ , the volume change accompanying a transition from one state to another, in terms of  $\Delta G$  starting with the definition given in Eq. 3.115.

[Solution](#)

- 5.16.** Derive an equation for the temperature dependence of the vapor pressure of a liquid (analogous to the integrated form of the Clausius-Clapeyron equation) assuming that the vapor has the equation of state  $PV = RT + M$  where  $M$  is a constant.

[Solution](#)

- 5.17.** Calculate the vapor pressure above liquid ethanol at 35.0 °C when Ar is added until the total pressure is 100 bar. The density of liquid ethanol at this temperature is 0.7767 kg dm<sup>-3</sup> and the true vapor pressure is 100.0 Torr.

[Solution](#)

- 5.18.** A solid exists in two forms, A and B, whose densities are 3.5155 g cm<sup>-3</sup> and 2.2670 g cm<sup>-3</sup>, respectively. If the standard Gibbs energy change for the reaction  $A \rightleftharpoons B$  is 240 kJ kg<sup>-1</sup>, find the pressure at which the two forms of the solid are in equilibrium at 25 °C. Assume that the volume change in going from A to B is independent of the pressure.

[Solution](#)

- 5.19.** What are the partial pressures of toluene (0.60 mole fraction) and benzene (mole fraction) in a solution at 60 °C? What is the total pressure in the vapor? The vapor pressures of the pure substances at 60 °C are as follows: toluene, 0.185 bar; benzene, 0.513 bar.

[Solution](#)

- 5.20.** The normal boiling point of ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) is 197 °C; its enthalpy of vaporization is 801 J mol<sup>-1</sup>. Estimate the temperature at which ethylene glycol will boil in a vacuum distillation if the system were maintained at 50 Torr.

[Solution](#)



**Raoult's Law, Equivalence of Units, and Partial Molar Quantities**

- 5.21.** Benzene and toluene form nearly ideal solutions. If, at 300 K,  $P^*$  (toluene) = 3.572 kPa and  $P^*$  (benzene) = 9.657 kPa, compute the vapor pressure of a solution containing 0.60 mol fraction of toluene. What is the mole fraction of toluene in the vapor over this liquid?

[Solution](#)

- 5.22.** Often it is important to express one unit of concentration in terms of another. Derive a general expression to find the mole fraction  $x_2$  in a two-component system where the molality is given as  $m_2$ .

[Solution](#)

- 5.23.** Assuming that commercially available automotive antifreeze is pure ethylene glycol (it actually also contains relatively small amounts of added rust inhibitors and a fluorescent dye that helps to differentiate a radiator leak from condensation from the air conditioner), in what ratio *by volume* will antifreeze and water have to be mixed in order to have a solution that freezes at  $-20.0\text{ }^\circ\text{C}$ ? What will be the boiling point of this solution at 1 atm pressure? (MW =  $62.02\text{ g mol}^{-1}$ , density =  $1.1088\text{ g cm}^{-3}$ .)

[Solution](#)

- \*5.24.** The familiar term *molarity* is now discouraged by IUPAC because of the danger of confusion with molality. In its place, *concentration* is defined as the amount of substance 2,  $n_2$ , dissolved in unit volume of solution. Derive a general relation to find  $x_2$  from the concentration  $c_2$ . Let the solution density be  $\rho$ .

[Solution](#)

- 5.25.** Show that if a solute follows Henry's law in the form of  $P_2 = k'x_2$ , then the solvent must follow Raoult's law. (*Hint:* The use of the Gibbs-Duhem equation might prove useful.)

[Solution](#)

- 5.26.** A  $1.0\text{ }m$  solution of NaCl in water produces a freezing point depression of approximately 3.7 K. How can we account for this observation?

[Solution](#)

- 5.27.** Derive a general expression to relate the molality  $m$  to concentration  $c_2$ .

[Solution](#)

- 5.28.** An amalgam of 1.152 g of a metal dissolved in 100.0 g of mercury is heated to boiling. The partial pressure of mercury vapor over the boiling mixture is 754.1 Torr and the total pressure is 768.8 Torr. Find the atomic weight of the metal and, therefore, its identity.

[Solution](#)

- \*5.29.** The volume of a solution of NaCl in water is given by the expression

$$V/\text{cm}^3 = 1002.874 + 17.8213 m + 0.87391 m^2 - 0.047225 m^3$$

where  $m$  is the molality. Assume that  $m \propto n_{\text{NaCl}}$  and that  $n_{\text{H}_2\text{O}} = 55.508 \text{ mol}$ , where  $V_{\text{H}_2\text{O}}^* = 18.068 \text{ cm}^3$ . Derive an analytical expression for the partial molar volume of  $\text{H}_2\text{O}$  in the solution.

[Solution](#)

- \*5.30.** The partial molar volume of component 2 in a solution may be written as

$$\begin{aligned} V_2 &= \left( \frac{\partial V}{\partial n_2} \right)_{n_1} \\ &= \frac{M_2}{\rho} - (M_1 n_1 + M_2 n_2) \frac{1}{\rho^2} \left( \frac{\partial \rho}{\partial n_2} \right)_{n_1} \end{aligned}$$

where  $n_1$  and  $M_1$  are amount and molar mass of component 1 and  $n_2$  and  $M_2$  represent the same quantities for component 2. The density is  $\rho$ . Rewrite the expression in terms of the mole fractions  $x_1$  and  $x_2$ .

[Solution](#)

- \*5.31.** Mikhail and Kimel, *J. Chem. Eng. Data*, 6, 533(1961), give the density of a water-methanol solution in  $\text{g cm}^{-3}$  at 298 K related to the mole fraction  $x_2$  of the methanol through the equation

$$\begin{aligned} \rho/\text{g cm}^{-3} &= 0.9971 - 0.28930x_2 + 0.29907x_2^2 \\ &\quad - 0.60876x_2^3 + 0.59438x_2^4 - 0.20581x_2^5 \end{aligned}$$

Using the equation developed in Problem 5.30, calculate  $V_2$  at 298 K when  $x_2 = 0.100$ .

[Solution](#)

- 5.32.** Beckmann and Faust [*Z. Physik. Chemie*, 89, 235(1915)] found that a solution of chloroform in acetone in which the mole fraction of the latter is 0.713 has a total vapor pressure of 220.5 Torr at 28.15 °C. The mole fraction of acetone in the vapor is 0.818. The vapor pressure of pure chloroform at this temperature is 221.8 Torr. Assuming that the vapor behaves ideally, calculate the activity and the activity coefficient of chloroform.

[Solution](#)

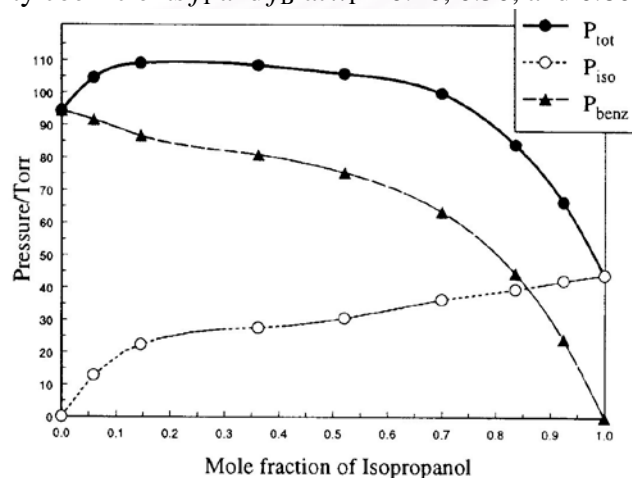
- 5.33.** When 12.5 g of A, a nonvolatile compound, is dissolved in 520.8 g of ethanol, the vapor pressure of the pure solvent, 56.18 Torr, is reduced to 55.24 Torr. Calculate the molar mass of compound A.

[Solution](#)

- 5.34.** The following data are for mixtures of isopropanol (I) in benzene (B) at 25 °C.

$x_I$	0	0.059	0.146	0.362				
$P_I$ (Torr)	0	12.9	22.4	27.6				
$P_{\text{tot}}$	94.4	104.5	109.0	108.4				
		0.521	0.700	0.836	0.924	1.0		
		30.5	36.4	39.5	42.2	44.0		
		105.8	99.8	84.0	66.4	44.0		

Does this solution exhibit positive or negative deviation from Raoult's law? From a pressure-composition plot, estimate the activities  $a_I$  and  $a_B$  and activity coefficients  $f_I$  and  $f_B$  at  $x_I = 0.20, 0.50$ , and  $0.80$ . [Data from Olsen and Washburn, *J. Phys. Chem.*, 41, 457(1937).]

[Solution](#)

- 5.35.** The vapor pressure of pure ethylene dibromide is 172 Torr and that of pure propylene dibromide is 128 Torr both at 358 K and 1 atm pressure. If these two components follow Raoult's law, estimate the total vapor pressure in kPa and the vapor composition in equilibrium with a solution that is 0.600 mol fraction propylene dibromide.

[Solution](#)

- 5.36.** Calculate Henry's law constant and the vapor pressure of pure liquid A (molar mass =  $89.5 \text{ g mol}^{-1}$ ) and that of 75.0 g of liquid A in solution with 1000 g of liquid B. Liquid B (molar mass =  $185 \text{ g mol}^{-1}$ ) has a pressure in this solution of 430 Torr and the total solution pressure is 520 Torr.

[Solution](#)

- \*5.37.** Henry's law constants  $k'$  for  $\text{N}_2$  and  $\text{O}_2$  in water at  $20.0^\circ\text{C}$  and 1 atm pressure are  $7.58 \times 10^4 \text{ atm}$  and  $3.88 \times 10^4 \text{ atm}$ , respectively. If the density of water at  $20.0^\circ\text{C}$  is  $0.9982 \text{ g cm}^{-3}$ , calculate (a) the equilibrium mole fraction and (b) the concentration of  $\text{N}_2$  and  $\text{O}_2$  in water exposed to air at  $20.0^\circ\text{C}$  and 1 atm total pressure. Assume in this case that air is 80.0 mol %  $\text{N}_2$  and 20.0 mol %  $\text{O}_2$ .

[Solution](#)

- 5.38.** Methane dissolves in benzene with a Henry's law constant of  $4.27 \times 10^5 \text{ Torr}$ . Calculate methane's molal solubility in benzene at  $25^\circ\text{C}$  if the pressure above benzene is 750 Torr. The vapor pressure of benzene is 94.6 Torr at  $25^\circ\text{C}$ .

[Solution](#)

### Thermodynamics of Solutions

- 5.39.** In a molar mass determination, 18.04 g of the sugar mannitol was dissolved in 100.0 g of water. The vapor pressure of the solution at 298 K was 2.291 kPa, having been lowered by 0.0410 kPa from the value for pure water. Calculate the molar mass of mannitol.

[Solution](#)

- 5.40.** A liquid has a vapor pressure of 40.00 kPa at 298.15 K. When 0.080 kg of an involatile solute is dissolved in 1 mol of the liquid, the new vapor pressure is 26.66 kPa. What is the molar mass of the solute? Assume that the solution is ideal.

[Solution](#)

- \*5.41.** Components 1 and 2 form an ideal solution. The pressure of pure component 1 is 13.3 kPa at 298 K, and the corresponding vapor pressure of component 2 is approximately zero. If the addition of 1.00 g of component 2 to 10.00 g of component 1 reduces the total vapor pressure to 12.6 kPa, find the ratio of the molar mass of component 2 to that of component 1.

[Solution](#)

- 5.42.** Pure naphthalene has a melting point of 353.35 K. Estimate the purity of a sample of naphthalene in mol %, if its freezing point is 351.85 K ( $K_f = 7.0 \text{ K kg mol}^{-1}$ ).

[Solution](#)

- 5.43.** Calculate the activity and activity coefficients for 0.330 mol fraction toluene in benzene. The vapor pressure of pure benzene is 9.657 kPa at 298 K.  $P_2^* = 3.572 \text{ kPa}$  for toluene. The vapor pressure for benzene above the solution is  $P_1 = 6.677 \text{ kPa}$  and for toluene  $P_2 = 1.214 \text{ kPa}$ .

[Solution](#)

- 5.44.** Calculate the mole fraction, activity, and activity coefficients for water when 11.5 g NaCl are dissolved in 100 g water at 298 K. The vapor pressure is 95.325 kPa.

[Solution](#)

- 5.45.** Determine the range for the Gibbs energy of mixing for an ideal 50/50 mixture at 300 K. How does this value limit  $\Delta_{\text{mix}}H$ ?

[Solution](#)

- 5.46.** The mole fraction of a nonvolatile solute dissolved in water is 0.010. If the vapor pressure of pure water at 293 K is 2.339 kPa and that of the solution is 2.269 kPa, calculate the activity and activity coefficient of water.

[Solution](#)

- \*5.47.** A nonideal solution contains  $n_A$  of substance A and  $n_B$  of substance B and the mole fractions of A and B are  $x_A$  and  $x_B$ . The Gibbs energy of the solution is given by the equation

$$G = n_A \mu_A^o + n_B \mu_B^o + RT(n_A \ln x_A + n_B \ln x_B) + C n_A n_B / (n_A + n_B)$$

where  $C$  is a constant and describes the pair interaction.

- a.** Derive an equation for  $\mu_A$  in the solution in terms of the quantities on the right-hand side. {Hint:  $(\partial \ln x_A / \partial n_A)_{n_B} = (1/n_A) - [1/(n_A + n_B)]$ . }

- b.** Derive a similar expression for the activity coefficient of A. Specify the conditions when the activity coefficient equals unity.

[Solution](#)

**Colligative Properties**

- 5.48.** Calculate the mole fraction solubility of naphthalene at 25 °C in a liquid with which it forms an ideal solution. The  $\Delta_{\text{fus}}H = 19.0 \text{ kJ mol}^{-1}$  for naphthalene at 25 °C. Its normal melting point is 80.2 °C.

[Solution](#)

- 5.49.** Using Henry's law, determine the difference between the freezing point of pure water and water saturated with air at 1 atm. For  $\text{N}_2$  at 298.15 K,

$$(k'')^{-1} = 2.17 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1}$$

For  $\text{O}_2$  at 298.15 K,

$$(k'')^{-1} = 1.02 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1}$$

[Solution](#)

- 5.50.** Using van't Hoff's equation, calculate the osmotic pressure developed if 6.00 g of urea,  $(\text{NH}_2)_2\text{CO}$ , is dissolved in 1.00  $\text{dm}^3$  of solution at 27 °C.

[Solution](#)

- 5.51.** The apparent value of  $K_f$  in 1.50-molal aqueous sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) solution is 2.17 K kg  $\text{mol}^{-1}$ . The solution does not behave ideally; calculate its activity and activity coefficient ( $\Delta_{\text{fus}}H^\circ = 6009.5 \text{ J mol}^{-1}$ ).

[Solution](#)

- 5.52.** A 0.85-g sample is dissolved in 0.150 kg of bromobenzene. Determine the molar mass of the solute if the solution boils at 429.0 K at 1 atm pressure. The normal boiling point of bromobenzene is 428.1 K and the boiling point elevation constant is 6.26 K kg  $\text{mol}^{-1}$ .

[Solution](#)

- \*5.53.** If in a colligative properties experiment a solute dissociates, a term  $i$  known as van't Hoff's factor, which is the total concentration of ions divided by the nominal concentration, must be included as a factor. Thus, for the lowering of the freezing point,  $\Delta_{\text{fus}}T = imK_f$ . Derive an expression that relates to the degree of dissociation  $\alpha$  and to  $\nu$ , the number of particles that would be produced if the solute were completely dissociated. Then calculate van't Hoff's  $i$  factor and  $\alpha$  for a 0.010-m solution of HCl that freezes at 273.114 K.

[Solution](#)



**5.54.** In an osmotic pressure experiment to determine the molar mass of a sugar, the following data were taken at 20 °C:

$\pi/\text{atm}$	2.59	5.06	7.61	12.75	18.13	23.72
$m_2 V^{-1}/\text{g dm}^{-3}$	33.5	65.7	96.5	155	209	259

Estimate the molar mass of the sugar. If the sugar is sucrose, what is the percentage error and why?

[Solution](#)

**5.55.** When 3.78 g of a nonvolatile solute is dissolved in 300.0 g of water, the freezing point depression is 0.646 °C. Calculate the molar mass of the compound.  $K_f = 1.856 \text{ K kg mol}^{-1}$ .

[Solution](#)

**5.56.** Calculate the elevation in the boiling point of water if 6.09 g of a nonvolatile compound with molar mass of  $187.4 \text{ g mol}^{-1}$  is dissolved in 250.0 g of water. Compare the values obtained using Eq. 5.125 and Eq. 5.126. The value of  $K_b = 0.541 \text{ K kg mol}^{-1}$ ;  $\Delta_{\text{vap}}H = 40.66 \text{ kJ mol}^{-1}$ .

[Solution](#)

**5.57.** Suppose that you find in the older literature the vapor pressure  $P$  of a liquid with molar mass of  $63.9 \times 10^{-3} \text{ kg mol}^{-1}$  listed with  $P$  in mmHg as

$$\log P = 5.4672 - 1427.3 T^{-1} - 3169.3 T^{-2}$$

The densities of the liquid and vapor phases are  $0.819 \text{ kg dm}^{-3}$  and  $3.15 \times 10^{-4} \text{ kg dm}^{-3}$ , respectively. Calculate the  $\Delta_{\text{vap}}H$  at the normal boiling point, 398.4 K. How do you handle the fact that  $P$  is listed in mmHg?

[Solution](#)

**5.58.** Calculate the osmotic pressure of seawater using the data of Table 5.5. Assume a temperature of 298 K and that the concentration of the additional salts not listed does not substantially contribute to the osmotic pressure.

[Solution](#)

### Essay Questions

**5.59.** Describe the form of a typical  $P\theta$  diagram and how the Gibbs-energy diagram may be generated for a one-component system. What is the requirement of stability for each region in the  $P\theta$  diagram?

- 5.60.** Detail the steps in going from the Clapeyron equation to the Clausius-Clapeyron equation. What specific assumptions are made?
- 5.61.** Explain why Trouton's rule, according to which the entropy of vaporization is  $88 \text{ J K}^{-1} \text{ mol}^{-1}$ , holds fairly closely for normal liquids.
- 5.62.** Describe three colligative properties and comment on their relative merits for the determination of molar masses of proteins.
- 5.63.** Show mathematically how the chemical potential is the driving force of diffusion for component A between two phases  $\alpha$  and  $\beta$ .
- 5.64.** Why do positive and negative deviations from Raoult's law occur?



**Solutions**

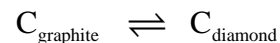
**5.1.** Diamonds have successfully been prepared by submitting graphite to high pressure. Calculate the approximate minimum pressure needed using  $\Delta_f G = 0$  for graphite and  $\Delta_f G = 2.90 \times 10^3 \text{ J mol}^{-1}$  for diamond. The densities of the two forms may be taken as independent of pressure and are  $2.25 \text{ g cm}^{-3}$  and  $3.51 \text{ g cm}^{-3}$ , respectively.

**Solution:**

Given:  $\Delta_f G = 0$ ,  $\Delta_f G = 2.90 \times 10^3 \text{ J mol}^{-1}$ ,  $\rho_{\text{graphite}} = 2.25 \text{ g cm}^{-3}$ ,  $\rho_{\text{diamond}} = 3.51 \text{ g cm}^{-3}$

Required:  $P_{\text{diamond}}$

The equilibrium presented in this problem is given by,



Using equation 3.119 we can obtain  $\Delta V$  and further solve to obtain  $P$ .

$$\left( \frac{\partial G}{\partial P} \right)_T = V, \text{ hence } \left( \frac{\partial \Delta G}{\partial \Delta P} \right)_T = \Delta V$$

$\Delta V$  can be obtained using the densities given in the problem.

$$\rho = \frac{n}{V}$$

$$V = \frac{n}{\rho}$$

To convert from molar volume, we multiply by the molar mass of carbon.

$$\Delta V = M \frac{n}{\Delta \rho}, \text{ let } n = 1 \text{ mol}$$

$$\Delta V = Mn \left( \frac{1}{\rho_{\text{graphite}}} - \frac{1}{\rho_{\text{diamond}}} \right)$$

$$\Delta V = (12.011 \text{ g mol}^{-1}) (1 \text{ mol}) \left( \frac{1}{2.25 \text{ g cm}^{-3}} - \frac{1}{3.51 \text{ g cm}^{-3}} \right)$$

$$\Delta V = 1.916 \text{ 285 } \cancel{\text{cm}^3} \times 10^{-6} \frac{\text{m}^3}{\cancel{\text{cm}^3}}$$

$$\Delta V = 1.916 \text{ 285} \times 10^{-6} \text{ m}^3$$

Using equation 3.119 we obtain,

$$\left( \frac{\partial \Delta G}{\partial \Delta P} \right)_T = \Delta V$$

$$\int_1^2 \partial \Delta G = \int_1^2 \Delta V \partial \Delta P$$

$$\Delta G_2 - \Delta G_1 = \Delta V (P_2 - P_1)$$

$$\frac{\Delta G_2 - \Delta G_1}{\Delta V} = (P_2 - P_1)$$

$$P_2 = \frac{\Delta G_2 - \Delta G_1}{\Delta V} + P_1,$$

$$\Delta G_2 = 0 \text{ at equilibrium}$$

$$P_2 = \frac{0 - 2.90 \times 10^3 \text{ J mol}^{-1}}{1.916 \text{ 285} \times 10^{-6} \text{ m}^3} + P_1$$

Under standard conditions, we use  $P_1$  as  $10^5 \text{ Pa}$ .

$$P_2 = \frac{0 - 2.90 \times 10^3 \text{ J mol}^{-1}}{1.916\,285 \times 10^{-6} \text{ m}^3} + 10^5 \text{ Pa}$$

$$P_2 = 1\,513\,444\,831 \text{ Pa}$$

$$P_2 = 1.51 \times 10^9 \text{ Pa} = 1.51 \times 10^4 \text{ bar}$$

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**5.2.** The molar entropy of vaporization of water is  $108.72 \text{ J K}^{-1}$  at 760 Torr. The corresponding densities of liquid water and water vapor are  $0.958 \text{ kg dm}^{-3}$  and  $5.98 \times 10^{-4} \text{ kg dm}^{-3}$ , respectively. Calculate the change of pressure for a one-degree change in temperature.

**Solution:**

Given:  $\Delta S = 108.72 \text{ J K}^{-1}$ ,  $P = 760 \text{ Torr}$ ,  $\rho_{\text{liquid}} = 0.958 \text{ kg dm}^{-3}$ ,  $\rho_{\text{vapor}} = 5.98 \times 10^{-4} \text{ kg dm}^{-3}$ ,

$$\Delta T = 1 \text{ }^{\circ}\text{C} = 1 \text{ K}$$

Required:  $\Delta P$

To solve this problem we can use Eq. 5.8 which defines the change in pressure over time.

$$\frac{dP}{dT} = \frac{S_m(\text{v}) - S_m(\text{l})}{V_m(\text{v}) - V_m(\text{l})} = \frac{\Delta S_m}{\Delta V_m}$$

This can also be rewritten as,

$$\frac{dP}{dT} = \frac{\Delta P}{\Delta T} = \frac{\Delta S_{\text{vaporization}}}{V_v - V_l}$$

To solve for  $\Delta P$ , we first need to obtain the values of  $V_v$  and  $V_l$ . These can be determined by using the densities given in the problem.

$$\rho = \frac{n}{V}$$

$$V = \frac{n}{\rho}$$

To convert from molar volume, we multiply by the molar mass of water.

$$V = M \frac{n}{\rho}, \text{ let } n = 1 \text{ mol}$$

$$V_l = \left( 2 \left( 1.007 \, 94 \times 10^{-3} \, \cancel{\text{kg}} \, \cancel{\text{mol}^{-1}} \right) + \left( 15.9994 \times 10^{-3} \, \cancel{\text{kg}} \, \cancel{\text{mol}^{-1}} \right) \right) \left( \frac{1 \, \cancel{\text{mol}}}{0.958 \, \cancel{\text{kg}} \, \text{dm}^{-3}} \right)$$

$$V_l = 18.805 \times 10^{-2} \, \text{dm}^3$$

$$V_v = \left( 2 \left( 1.007 \, 94 \times 10^{-3} \, \cancel{\text{kg}} \, \cancel{\text{mol}^{-1}} \right) + \left( 15.9994 \times 10^{-3} \, \cancel{\text{kg}} \, \cancel{\text{mol}^{-1}} \right) \right) \left( \frac{1 \, \cancel{\text{mol}}}{5.98 \times 10^{-4} \, \cancel{\text{kg}} \, \text{dm}^{-3}} \right)$$

$$V_v = 30.126 \, \text{dm}^3$$

Rearranging Eq. 5.8 we can solve for  $\Delta P$  which yields:

$$\Delta P = \frac{\Delta S_{\text{vaporization}}}{V_v - V_l} \Delta T$$

$$\Delta P = \frac{108.72 \, \text{J} \, \cancel{\text{K}}^{-1}}{30.126 \, \text{dm}^3 - 18.805 \times 10^{-2} \, \text{dm}^3} (1 \, \cancel{\text{K}})$$

$$\Delta P = 3.6111 \left( \times 10^3 \, \text{m}^{-3} \, \cancel{\text{dm}^3} \right) \, \cancel{\text{J}} \, \cancel{\text{dm}^{-3}}$$

$$\Delta P = 3.6111 \times 10^3 \, \text{J} \, \text{m}^{-3}$$

where  $1 \, \text{J} = 1 \, \text{kg} \, \text{m}^2 \, \text{s}^{-2}$  and  $1 \, \text{Pa} = 1 \, \text{kg} \, \text{m}^{-1} \, \text{s}^{-2}$

$$\Delta P = 3.6111 \times 10^3 \, (\text{kg} \, \text{m}^2 \, \text{s}^{-2}) \, \text{m}^{-3}$$

$$\Delta P = 3.6111 \times 10^3 \, \text{kg} \, \text{m}^{-1} \, \text{s}^{-2}$$

$$\boxed{\Delta P = 3.61 \times 10^3 \, \text{Pa}}$$

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**5.3.** Calculate the heat of vaporization of water at 373.15 K and 101.325 kPa using the Clausius-Clapeyron equation. The vapor pressure of water is 3.17 kPa at 298.15 K. Compare your answer to the CRC Handbook<sup>2</sup> value.

**Solution:**

Given:  $T = 373.15\text{ K}$ ,  $P = 101.325\text{ kPa}$ ,  $P_{\text{vap}} = 3.17\text{ kPa}$  at  $T = 298.15\text{ K}$

Required:  $\Delta_{\text{vap}}H_m$

The Clausius-Clapeyron equation is given by Eq. 5.16,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Rearranging and solving for  $\Delta_{\text{vap}}H_m$  gives,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{T_2 - T_1}{T_2 T_1} \right)$$

$$\Delta_{\text{vap}}H_m = R \ln \frac{P_2}{P_1} \left( \frac{T_2 T_1}{T_2 - T_1} \right)$$

$$\Delta_{\text{vap}}H_m = (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \ln \left( \frac{101.325\text{ kPa}}{3.17\text{ kPa}} \right) \left( \frac{(373.15\text{ K})(298.15\text{ K})}{373.15\text{ K} - 298.15\text{ K}} \right)$$

$$\Delta_{\text{vap}}H_m = 42\,731.332\text{ J mol}^{-1}$$

$$\boxed{\Delta_{\text{vap}}H_m = 42.7\text{ kJ mol}^{-1}}$$

The CRC Handbook value is  $40.57\text{ kJ mol}^{-1}$ .

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<sup>2</sup>Handbook of Chemistry and Physics, 82nd ed., D. R. Lide, Ed., Boca Raton, FL: CRC Press, 2001.

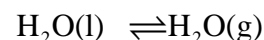
**5.4.** Liquid water and vapor are in equilibrium at the triple point of water (0.00603 atm and 273.16 K). Assuming that the enthalpy of vaporization of water does not change over the temperature range considered, calculate the equilibrium vapor pressure of water at 373.15 K. Comment on the assumption made here. ( $\Delta_{\text{vap}}H^\circ = 40\,656 \text{ J mol}^{-1}$  at 1 atm.)

**Solution:**

Given:  $P_{\text{triple}} = 0.00603 \text{ atm}$ ,  $T_{\text{triple}} = 273.16 \text{ K}$ ,  $\Delta_{\text{vap}}H^\circ = 40\,656 \text{ J mol}^{-1}$  at 1 atm

Required:  $P_{\text{vap}}$  at  $T = 373.15 \text{ K}$

The equilibrium presented in this problem is given by,



The Clausius-Clapeyron equation is given by Eq. 5.16,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Rearranging and solving for  $P_{\text{vap}}$  gives,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\frac{P_2}{P_1} = e^{\frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$P_{\text{vap}} = P_{\text{triple}} e^{\frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$P_{\text{vap}} = (0.00603 \text{ atm}) e^{\frac{40\,656 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{273.16 \text{ K}} - \frac{1}{373.15 \text{ K}} \right)}$$

$$P_{\text{vap}} = (0.00603 \text{ atm}) e^{4.796\,721\,772}$$

$$P_{\text{vap}} = 0.730\,309\,767 \text{ atm}$$

$$\boxed{P_{\text{vap}} = 0.730 \text{ atm}}$$

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- 5.5.** Estimate the vapor pressure of iodine under an external pressure of  $101.3 \times 10^6$  Pa at 313.15 K. The density of iodine is  $4.93 \text{ g cm}^{-3}$ . The vapor pressure at 101.3 kPa is 133 Pa.

**Solution:**

Given:  $T = 313.15 \text{ K}$ ,  $\rho = 4.93 \text{ g cm}^{-3}$ ,  $P_{\text{ext}} = 101.3 \text{ kPa}$ ,  $P_{\text{vap}} = 133 \text{ Pa}$

Required:  $P_{\text{vap}}$  at  $P_{\text{ext}} = 101.3 \times 10^6 \text{ Pa}$

Since the vapor pressure varies with external pressure, we use Eq. 5.23 to solve this problem.

$$\ln \frac{P_t}{P_v} = \frac{V_m(l)}{RT} (P_t - P_v)$$

This can be rewritten as,

$$\ln \frac{P_1^g}{P_2^g} = \frac{V_m(l)}{RT} (P_1 - P_2)$$

To obtain  $V_m$  we use the density given in the problem.

$$\rho = \frac{n}{V}$$

$$V = \frac{n}{\rho}$$

To convert from molar volume, we need to multiply by the molar mass of water.



$$V = M \frac{n}{\rho}, \text{ let } n = 1 \text{ mol}$$

$$V_m = \left( 2 \left( 126.904 \text{ 47 } \cancel{\text{g mol}^{-1}} \right) \right) \left( \frac{1 \text{ mol}}{4.93 \cancel{\text{g cm}^{-3}}} \right)$$

$$V_m = 51.482 \text{ 543 61 } \cancel{\text{cm}^3} \times 10^{-6} \frac{\text{m}^3}{\cancel{\text{cm}^3}}$$

$$V_m = 5.148 \text{ 254 361 } \times 10^{-5} \text{ m}^3$$

From Eq. 5.23 we can solve for  $P_{\text{vap}}$

$$\ln \frac{P_1^g}{P_2^g} = \frac{5.148 \text{ 254 361 } \times 10^{-5} \cancel{\text{m}^3}}{\left( 8.3145 \cancel{\text{J K}^{-1} \text{ mol}^{-1}} \right) \left( 313.15 \cancel{\text{K}} \right)} \left( 101.3 \times 10^6 \cancel{\text{Pa}} - 101.3 \times 10^3 \cancel{\text{Pa}} \right)$$

$$\frac{P_1^g}{P_2^g} = e^{2.000 \text{ 996 716}}$$

$$\frac{P_1^g}{P_2^g} = 7.396 \text{ 424 563}$$

At 101.3 kPa, the pressure is 133 Pa. Therefore at  $101.3 \times 10^3$  kPa the vapor pressure is  $7.396 \text{ 424 563} \times 133$  Pa

$$P_{\text{vap}} = 7.396 \text{ 424 563} \times 133 \text{ Pa}$$

$$P_{\text{vap}} = 983.724 \text{ 467 Pa}$$

$$\boxed{P_{\text{vap}} = 984 \text{ Pa}}$$

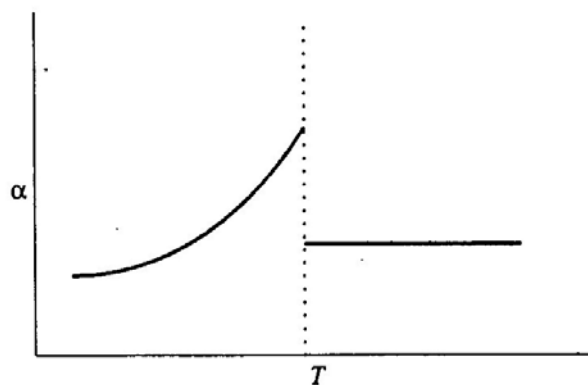
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- 5.6. The cubic expansion coefficient is given by  $\alpha = 1/V (\partial V/\partial T)_P$ . According to Ehrenfest's or Tisza's theory, find the order of the transition. Suggest what a plot of  $\alpha$  against  $T$  would look like near the transition point.

**Solution:**

The cubic expansion coefficient is a second order transition since it can be expressed as  $\alpha = \frac{1}{V} \left[ \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right)_T \right]_P$



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**5.7.** The vapor pressure of *n*-propanol is 1.94 kPa at 293 K and 31.86 kPa at 343 K. What is the enthalpy of vaporization?

**Solution:**

Given:  $P_1 = 1.94$  kPa,  $T_1 = 293$  K,  $P_2 = 31.86$  kPa,  $T_2 = 343$  K

Required:  $\Delta_{\text{vap}} H_m$

To obtain the enthalpy of vaporization, we must use the Clausius-Clapeyron equation, in the form of Eq. 5.16:

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Rearranging, we can solve for  $\Delta_{\text{vap}} H_m$ ,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Delta_{\text{vap}} H_m = \left( \frac{T_1 T_2}{T_2 - T_1} \right) R \ln \frac{P_2}{P_1}$$

$$\Delta_{\text{vap}} H_m = \left( \frac{(293 \text{ K})(343 \text{ K})}{343 \text{ K} - 293 \text{ K}} \right) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{31.86 \text{ kPa}}{1.94 \text{ kPa}} \right)$$

$$\Delta_{\text{vap}} H_m = 46\,771.202\,01 \text{ J mol}^{-1}$$

$$\boxed{\Delta_{\text{vap}} H_m = 46.8 \text{ kJ mol}^{-1}}$$

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**5.8.** The compound 2-hydroxybiphenyl (*o*-phenylphenol) boils at 286 °C under 101.325 kPa and at 145 °C under a reduced pressure of 14 Torr. Calculate the value of the molar enthalpy of vaporization. Compare this value to that given in the CRC Handbook.

**Solution:**

Given:  $T_1 = 286^\circ\text{C} = 559.15\text{ K}$ ,  $P_1 = 101.325\text{ kPa}$ ,  $T_2 = 145^\circ\text{C} = 418.15\text{ K}$ ,  $P_2 = 14\text{ Torr}$

Required:  $\Delta_{\text{vap}} H_m$

To obtain the enthalpy of vaporization, we must use the Clausius-Clapeyron equation, in the form of Eq. 5.16:

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Rearranging, we can solve for  $\Delta_{\text{vap}} H_m$ ,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Delta_{\text{vap}} H_m = \left( \frac{T_1 T_2}{T_2 - T_1} \right) R \ln \frac{P_2}{P_1}$$

$$\Delta_{\text{vap}} H_m = \left( \frac{(559.15\text{ K})(418.15\text{ K})}{418.15\text{ K} - 559.15\text{ K}} \right) (8.3145\text{ J K}^{-1}\text{ mol}^{-1})$$

$$\times \ln \left( \frac{14\text{ Torr}}{760\text{ Torr}} \times \frac{101.325\text{ Pa}}{101.325\text{ Pa}} \right)$$

$$\Delta_{\text{vap}} H_m = 55\,069.851\,64\text{ J mol}^{-1}$$

$$\boxed{\Delta_{\text{vap}} H_m = 55\text{ kJ mol}^{-1}}$$

The value for  $\Delta_{\text{vap}} H_m$  in the CRC Handbook is 71.02 kJ mol<sup>-1</sup>. The error is large, but considering the relative molecular mass of the compound, its high boiling point, and the wide range of  $T$  and  $P$  involved in the calculation, it is not surprising that the error is so large.

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- 5.9.** Using Trouton's rule, estimate the molar enthalpy of vaporization of *n*-hexane, the normal boiling point of which is 342.10 K. Compare the value obtained to the value  $31.912 \text{ kJ mol}^{-1}$  obtained in vapor pressure studies.

**Solution:**

Given:  $T = 342.10 \text{ K}$ ,  $\Delta_{\text{vap}}H_m = 31.912 \text{ kJ mol}^{-1}$

Required:  $\Delta_{\text{vap}}H_m$

Trouton's rule is given by Eq. 5.18:

$$\frac{\Delta_{\text{vap}}H_m}{T_b} = \Delta_{\text{vap}}S_m \approx 88 \text{ J K}^{-1} \text{ mol}^{-1}$$

Rearranging, we can solve for  $\Delta_{\text{vap}}H_m$ ,

$$T = 110.62^\circ\text{C} = 383.77 \text{ K}, \Delta_{\text{vap}}H_m = 31.912 \text{ kJ mol}^{-1}$$

We can compare this value with the value obtained in vapor pressure studies by calculating the percent error.

$$\% \text{ error} = \frac{31.912 \times 10^3 \text{ J mol}^{-1} - 30\,104.8 \text{ J mol}^{-1}}{31.912 \times 10^3 \text{ J mol}^{-1}} \times 100\%$$

$$\% \text{ error} = 5.663\,073\%$$

$$\boxed{\% \text{ error} = 5.6631\%}$$

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**5.10.** The normal boiling point of toluene is 110.62 °C. Estimate its vapor pressure at 80.00 °C assuming that toluene obeys Trouton's rule.

**Solution:**

Given:  $T_B = 110.62^\circ\text{C} = 383.77\text{ K}$ ,  $T = 80.00^\circ\text{C} = 353.15\text{ K}$

Required:  $P_{\text{vap}}$

Trouton's rule is given by Eq. 5.18:

$$\frac{\Delta_{\text{vap}} H_m}{T_b} = \Delta_{\text{vap}} S_m \approx 88 \text{ J K}^{-1} \text{ mol}^{-1}$$

Rearranging, we can solve for  $\Delta_{\text{vap}} H_m$  at  $T_B = 110.62^\circ\text{C}$ ,

$$\Delta_{\text{vap}} H_m = (88 \text{ J K}^{-1} \text{ mol}^{-1}) T_B$$

$$\Delta_{\text{vap}} H_m = (88 \text{ J K}^{-1} \text{ mol}^{-1}) (383.77 \text{ K})$$

$$\Delta_{\text{vap}} H_m = 33\,771.76 \text{ J mol}^{-1}$$

Using this value for  $\Delta_{\text{vap}} H_m$ , we can obtain  $P_{\text{vap}}$  from Eq. 5.16 the Clausius-Clapeyron equation. This can then be rearranged to obtain,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$P_2 = P_1 e^{\frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

Where  $P_1 = 1 \text{ atm}$  under standard conditions.

$$P_2 = (1 \text{ atm}) e^{\left( \frac{33771.76 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \left( \frac{1}{383.77 \text{ K}} - \frac{1}{353.15 \text{ K}} \right)}$$

$$P_2 = 0.399444 \text{ atm}$$

$$\boxed{P_2 = 0.3994 \text{ atm}}$$

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**5.11.** 2-Propanone (acetone) boils at 329.35 K at 1 atm of pressure. Estimate its boiling point at 98.5 kPa using Crafts' rule.

**Solution:**

Given:  $T_B = 329.35$  K,  $P = 1$  atm = 101.325 kPa,  $P = 98.5$  kPa

Required:  $T$

Crafts' rule is given by Eq. 5.19,

$$\frac{\Delta P}{\Delta T} = \frac{\Delta_{\text{vap}} H_m}{T_B} \times \frac{P}{RT_B}$$

First we can solve for  $\Delta T$  then we will be able to obtain  $T$ .

$$\Delta T = \left( \frac{RT_B}{P} \right) \left( \frac{T_B}{\Delta_{\text{vap}} H_m} \right) \Delta P$$

$$\Delta T = \left( \frac{(329.35 \text{ K})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})}{98.5 \times 10^3 \text{ Pa}} \right) \left( \frac{1}{88 \text{ J K}^{-1} \text{ mol}^{-1}} \right) (98500 \text{ Pa} - 101325 \text{ Pa})$$

$$\Delta T = -0.892469 \text{ K}$$

$T$  is given by,

$$T = 329.35 \text{ K} - 0.892469 \text{ K}$$

$$T = 328.457531 \text{ K}$$

$$\boxed{T = 328 \text{ K}}$$

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- 5.12.** The variation of the equilibrium vapor pressure with temperature for liquid and solid chlorine in the vicinity of the triple point is given by

$$\ln P_l = \frac{-2661}{T} + 22.76,$$

$$\ln P_s = \frac{-3755}{T} + 26.88.$$

Use  $P$ /pascal in the equations. Calculate the triple point pressure and temperature.

**Solution:**

Given:

Required:  $P_{\text{triple}}$ ,  $T_{\text{triple}}$

At the triple point, the two vapor pressures must be equal since the liquid, solid, and vapor are all in equilibrium with each other. Therefore we can say that,

$$\frac{-2661}{T_{\text{triple}}} + 22.76 = \frac{-3755}{T_{\text{triple}}} + 26.88$$

Solving the above expression for  $T_{\text{triple}}$  we obtain;

$$\frac{-2661}{T_{\text{triple}}} + 22.76 = \frac{-3755}{T_{\text{triple}}} + 26.88$$

$$\frac{-2661}{T_{\text{triple}}} + \frac{3755}{T_{\text{triple}}} = 4.12$$

$$-2661 + 3755 = 4.12 T_{\text{triple}}$$

$$T_{\text{triple}} = 270.388 \text{ 349 5 K}$$

$$\boxed{T_{\text{triple}} = 270.4 \text{ K}}$$

To obtain  $P_{\text{triple}}$ , we use the value for  $T_{\text{triple}}$  and one of the equations given in the problem. Both will give the same answer.

$$\ln P_{\text{triple}} = \frac{-2661}{270.388 \text{ 349 5 K}} + 22.76$$

$$P_{\text{triple}} = e^{\frac{-2661}{270.388 \text{ 349 5 K}} + 22.76}$$

$$P_{\text{triple}} = 407 \text{ 827.529 Pa}$$

Similarly,

$$\ln P_{\text{triple}} = \frac{-3755}{270.388 \text{ 349 5 K}} + 26.88$$

$$P_{\text{triple}} = 407 \text{ 827.529 Pa}$$

$$\boxed{P_{\text{triple}} = 407.8 \text{ kPa}}$$

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**5.13.** The boiling point of water at 102.7 kPa is 373.52 K. Calculate the value at 101.325 kPa (1 atm) using Crafts' rule.

**Solution:**

Given:  $P = 102.7$  kPa,  $T_B = 373.52$  K,  $P = 101.325$  kPa

Required:  $T$

Crafts' rule is given by Eq. 5.19:

$$\frac{\Delta P}{\Delta T} = \frac{\Delta_{\text{vap}} H_m}{T_B} \times \frac{P}{RT_B}$$

First we can solve for  $\Delta T$  which will then enable us to determine the value of  $T$ .

$$\Delta T = \left( \frac{RT_B}{P} \right) \left( \frac{T_B}{\Delta_{\text{vap}} H_m} \right) \Delta P$$

$$\Delta T = \left( \frac{(373.52 \text{ K})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})}{102.7 \times 10^3 \text{ Pa}} \right) \left( \frac{1}{88 \text{ J K}^{-1} \text{ mol}^{-1}} \right) (101.325 \text{ Pa} - 102.7 \times 10^3 \text{ Pa})$$

$$\Delta T = -0.472498 \text{ K}$$

$T$  is given by,

$$T = 373.52 \text{ K} - 0.472498 \text{ K}$$

$$T = 373.047502 \text{ K}$$

$$\boxed{T = 373.05 \text{ K}}$$

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**5.14.** The vapor pressure of water at 27.5 °C, a calibration temperature for glassware used in warmer climates, is 27.536 Torr under its own vapor pressure. Calculate the vapor pressure of water under an air pressure of 1.00 atm. Assume that air is inert. The density of water at 27.5 °C is 996.374 g dm<sup>-3</sup>.

**Solution:**

Given:  $T = 27.5\text{ °C} = 300.65\text{ K}$ ,  $P = 27.536\text{ Torr}$ ,  $P = 1.00\text{ atm}$ ,  $\rho = 996.374\text{ g dm}^{-3}$

Required:  $P_{\text{vap}}$

To calculate  $P_{\text{vap}}$  we may use Eq. 5.23 which states that:

$$\ln \frac{P}{P_v} = \frac{V_m(l)}{RT} (P_t - P_v)$$

Rearranging this expression to isolate for the vapour pressure gives,

$$P_{\text{vap}} = P_v e^{\frac{V_m(l)}{RT} (P_t - P_v)}$$

$$\text{where } V_m = \frac{M}{\rho}$$

$$V_m = \frac{(2(1.007\,94\text{ g mol}^{-1}) + (15.9994\text{ g mol}^{-1}))}{996.374\text{ g dm}^{-3}}$$

$$V_m = 0.018\,080\,841\,1\text{ dm}^3\text{ mol}^{-1}$$

$$P_{\text{vap}} = (27.536\text{ Torr}) e^{\frac{0.018\,080\,841\,1\text{ dm}^3\text{ mol}^{-1}}{(0.082\,06\text{ atm dm}^3\text{ K}^{-1}\text{ mol}^{-1} \times 760\text{ Torr atm}^{-1})(300.65\text{ K})}} (760\text{ Torr} - 27.536\text{ Torr})$$

$$P_{\text{vap}} = (27.536\text{ Torr}) e^{7.063152\,747 \times 10^{-4}}$$

$$P_{\text{vap}} = 27.555\,455\,97\text{ Torr}$$

$$\boxed{P_{\text{vap}} = 27.555\text{ Torr}}$$

This is a small correction, but may be necessary for accurate work.

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**5.15.** Following the derivation of the expression for  $\Delta S$  in terms of  $\Delta G$  in Eq. 3.161, derive an expression for  $\Delta V$ , the volume change accompanying a transition from one state to another, in terms of  $\Delta G$  starting with the definition given in Eq. 3.115.

**Solution:**

Given: Eq. 3.161, Eq. 3.115

Required: an expression for  $\Delta V$

Eq. 3.115 is given by the following expression:

$$dG = V dP - S dT = \left( \frac{\partial G}{\partial P} \right)_T dP + \left( \frac{\partial G}{\partial T} \right)_P dT$$

Recognize that a change of state occurs at constant temperature. Therefore, differentiating Eq. 3.115 with respect to  $P$  at constant temperature, we obtain the following from Eq. 3.119.

$$\left( \frac{\partial G}{\partial P} \right)_T = V$$

Now for a change of state, where  $G_f - G_i = \Delta G$ , there will be a corresponding change in volume,

$$\boxed{\left( \frac{\partial \Delta G}{\partial P} \right)_T = \Delta V}$$

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**5.16.** Derive an equation for the temperature dependence of the vapor pressure of a liquid (analogous to the integrated form of the Clausius-Clapeyron equation) assuming that the vapor has the equation of state  $PV = RT + M$  where  $M$  is a constant.

**Solution:**

Given:  $PV = RT + M$  where  $M$  is a constant

Required: expression for temperature dependence of the vapor pressure of a liquid

The general Clausius-Clapeyron equation, is given by Eq. 5.9 which states that:

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

Rearranging the equation of state for vapor and substituting gives,

$$PV = RT + M$$

$$V = \frac{RT + M}{P}$$

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}} H_m}{T \left( \frac{RT + M}{P} \right)}$$

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}} H_m P}{T (RT + M)}$$

$$\frac{dP}{P} = \frac{\Delta_{\text{vap}} H_m dT}{T (RT + M)}$$

Expanding the denominator yields,

$$\frac{1}{T(RT + M)} = \frac{1}{MT} - \frac{R}{M(RT + M)}$$

Therefore we obtain,

$$\frac{dP}{P} = \Delta_{\text{vap}} H_m dT \left( \frac{1}{MT} - \frac{R}{M(RT + M)} \right)$$

$$\frac{dP}{P} = \frac{\Delta_{\text{vap}} H_m dT}{MT} - \frac{R}{M} \frac{\Delta_{\text{vap}} H_m dT}{(RT + M)}$$

Integrating the above expression, and cancelling terms as necessary, gives,

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{M} \ln \frac{T_2}{T_1} - \frac{\cancel{R}}{M} \frac{\Delta_{\text{vap}} H_m}{\cancel{R}} \ln \frac{RT_2 + M}{RT_1 + M}$$

$$\boxed{\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H_m}{M} \ln \frac{T_2}{T_1} \left( \frac{RT_1 + M}{RT_2 + M} \right)}$$

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**5.17.** Calculate the vapor pressure above liquid ethanol at 35.0 °C when Ar is added until the total pressure is 100 bar. The density of liquid ethanol at this temperature is 0.7767 kg dm<sup>-3</sup> and the true vapor pressure is 100.0 Torr.

**Solution:**

Given: Ethanol, C<sub>2</sub>H<sub>5</sub>OH,  $P_{\text{total}} = 100 \text{ bar}$ ,  $\rho = 0.7767 \text{ kg dm}^{-3}$ ,  $P_{\text{true}} = 100.0 \text{ Torr}$

Required:  $P_{\text{vap}}$  at  $T_{\text{ext}} = 35^\circ\text{C} = 308.15 \text{ K}$

To calculate  $P_{\text{vap}}$  we must use Eq. 5.23 which states that:

$$\ln \frac{P}{P_v} = \frac{V_m(l)}{RT} (P_t - P_v)$$

Rearranging the above to isolate for the vapor pressure yields;

$$P_{\text{vap}} = P_v e^{\frac{V_m(l)}{RT} (P_t - P_v)}$$

$$\text{where } V_m = \frac{M}{\rho}$$

$$V_m = \frac{(2(12.011 \cancel{\text{g}} \text{ mol}^{-1}) + 6(1.00794 \cancel{\text{g}} \text{ mol}^{-1}) + (15.9994 \cancel{\text{g}} \text{ mol}^{-1}))}{776.7 \cancel{\text{g}} \text{ dm}^{-3}}$$

$$V_m = 0.0593138149 \cancel{\text{dm}^3} \text{ mol}^{-1} \times 10^{-3} \frac{\text{m}^3}{\cancel{\text{dm}^3}}$$

$$V_m = 5.93138149 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$P_{\text{vap}} = (100 \text{ Torr}) e^{\left( \frac{5.93138149 \times 10^{-5} \cancel{\text{m}^3} \cancel{\text{mol}^{-1}}}{(8.3145 \text{ J K}^{-1} \cancel{\text{mol}^{-1}})(308.15 \text{ K})} \right) \left( 100 \text{ bar} \times \frac{10^5 \text{ Pa}}{1 \cancel{\text{bar}}} - 100 \cancel{\text{Torr}} \times \frac{101325 \text{ Pa}}{760 \cancel{\text{Torr}}} \right)}$$

$$P_{\text{vap}} = (100 \text{ Torr}) e^{0.2311948469}$$

$$P_{\text{vap}} = 126.0104743 \text{ Torr}$$

$$\boxed{P_{\text{vap}} = 126 \text{ Torr}}$$

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**5.18.** A solid exists in two forms, A and B, whose densities are  $3.5155 \text{ g cm}^{-3}$  and  $2.2670 \text{ g cm}^{-3}$ , respectively. If the standard Gibbs energy change for the reaction  $A \rightleftharpoons B$  is  $240 \text{ kJ kg}^{-1}$ , find the pressure at which the two forms of the solid are in equilibrium at  $25^\circ\text{C}$ . Assume that the volume change in going from A to B is independent of the pressure.

**Solution:**

Given:  $\rho_A = 3.5155 \text{ g cm}^{-3}$ ,  $\rho_B = 2.2670 \text{ g cm}^{-3}$ ,  $\Delta G = 240 \text{ kJ kg}^{-1}$ ,  $T = 25^\circ\text{C} = 298.15 \text{ K}$

Required:  $P$  at equilibrium

We can use the result obtained in problem 5.15 to solve this problem.

$$\left( \frac{\partial \Delta G}{\partial P} \right)_T = \Delta V$$

The change in volume can be calculated from the densities given above.

$$\Delta V = \frac{1}{\Delta \rho}$$

$$\Delta V = \left( \frac{1}{3.5155 \text{ g cm}^{-3}} - \frac{1}{2.2670 \text{ g cm}^{-3}} \right)$$

$$\Delta V = -0.156\,657\,042\,9 \cancel{\text{ g}^{-1}} \cancel{\text{ cm}^3} \times 10^{-3} \frac{\text{ m}^3 \text{ kg}^{-1}}{\cancel{\text{ cm}^3} \cancel{\text{ g}^{-1}}}$$

$$\Delta V = -0.156\,657\,042\,9 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$$

Solving for  $P$  we obtain;

$$\int_1^2 d\Delta G = \int_{P_1}^{P_2} \Delta V dP$$

$$\Delta G_2 - \Delta G_1 = \Delta V (P_2 - P_1)$$

Let state 1 be the standard state, and state 2 be the equilibrium state. At equilibrium,  $\Delta G=0$ , therefore the expression becomes,

$$\cancel{\Delta G} - \Delta G^\circ = \Delta V (P - P^\circ)$$

$$\frac{-\Delta G^\circ}{\Delta V} = (P - P^\circ)$$

$$P = \frac{-\Delta G^\circ}{\Delta V} + P^\circ$$

$$P = \frac{-(240 \times 10^3 \text{ J } \cancel{\text{kg}^{-1}})}{(-0.156 \ 657 \ 042 \ 9 \times 10^{-3} \text{ m}^3 \cancel{\text{kg}^{-1}})} + 10^5 \text{ Pa}$$

$$P = 1532009002 \text{ J m}^{-3} + 10^5 \text{ Pa}$$

where  $1 \text{ J} = \text{kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = \text{kg m}^{-1} \text{ s}^{-2}$

$$\frac{1 \text{ J}}{1 \text{ m}^3} = \frac{\text{kg m}^2 \text{ s}^{-2}}{\text{m}^3} = \text{kg m}^{-1} \text{ s}^{-2} = 1 \text{ Pa}$$

$$P = 1532009002 \text{ Pa} + 10^5 \text{ Pa}$$

$$P = 1532109002 \text{ Pa}$$

$$\boxed{P = 1.53 \times 10^9 \text{ Pa}}$$

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**5.19.** What are the partial pressures of toluene (0.60 mole fraction) and benzene (mole fraction) in a solution at 60 °C? What is the total pressure in the vapor? The vapor pressures of the pure substances at 60 °C are as follows: toluene, 0.185 bar; benzene, 0.513 bar.

**Solution:**

Given:  $x_{\text{toluene}} = 0.60$ ,  $x_{\text{benzene}} = 0.40$ ,  $T = 60^\circ\text{C} = 333.15\text{ K}$ ,  $P_{\text{toluene}}^* = 0.185\text{ bar}$ ,  $P_{\text{benzene}}^* = 0.513\text{ bar}$

Required:  $P_{\text{total}}$

The total pressure is given by the sum of partial pressures of each of the components in a mixture:

$$P_{\text{total}} = P_{\text{toluene}} + P_{\text{benzene}}$$

Raoult's Law is given by Eq. 5.26, and can be used to solve for  $P_{\text{total}}$ .

$$P_1 = x_1 P_1^*; \quad P_2 = x_2 P_2^*$$

$$P_{\text{toluene}} = 0.60(0.185\text{ bar})$$

$$P_{\text{toluene}} = 0.111\text{ bar}$$

$$P_{\text{benzene}} = 0.40(0.513\text{ bar})$$

$$P_{\text{benzene}} = 0.2052\text{ bar}$$

$$P_{\text{total}} = 0.111\text{ bar} + 0.2052\text{ bar}$$

$$P_{\text{total}} = 0.3162\text{ bar}$$

$$\boxed{P_{\text{total}} = 0.316\text{ bar}}$$

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**5.20.** The normal boiling point of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) is  $197\text{ }^\circ\text{C}$ ; its enthalpy of vaporization is  $801\text{ J mol}^{-1}$ . Estimate the temperature at which ethylene glycol will boil in a vacuum distillation if the system were maintained at 50 Torr.

**Solution:**

Given: ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ),  $T_B = 197\text{ }^\circ\text{C} = 470\text{ K}$ ,  $\Delta_{\text{vap}}H = 801\text{ J mol}^{-1}$

Required:  $T_B$  at  $P = 50\text{ Torr}$

To obtain the temperature, we must use the Clausius-Clapeyron equation, in the form of Eq. 5.16 which states that:

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

First, we can determine the molar enthalpy of vaporization by multiplying the enthalpy of vaporization by the molar mass of ethylene glycol.

$$\Delta_{\text{vap}}H_m = \Delta_{\text{vap}}H \times M$$

$$\Delta_{\text{vap}}H_m = \left( 801\text{ J g}^{-1} \right) \times \left( \left( 2 \left( 12.011\text{ g mol}^{-1} \right) + 6 \left( 1.007\text{ 94 g mol}^{-1} \right) + 2 \left( 15.9994\text{ g mol}^{-1} \right) \right) \right)$$

$$\Delta_{\text{vap}}H_m = 49\text{ 716.820 44 J mol}^{-1}$$

By making the appropriate substitutions into Eq. 5.16 we obtain,

$$\ln \frac{760 \text{ Torr}}{50 \text{ Torr}} = \frac{(49\,716.820\,44 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} \left( \frac{1}{T_1} - \frac{1}{470 \text{ K}} \right)$$

$$\ln \frac{760}{50} \left( \frac{(8.3145 \text{ K}^{-1})}{(49\,716.820\,44)} \right) + \frac{1}{470 \text{ K}} = \frac{1}{T_1}$$

$$\frac{1}{T_1} = 0.002\,582\,761\,3 \text{ K}^{-1}$$

$$T_1 = 387.182\,508\,7 \text{ K}$$

$$\boxed{T_1 = 387 \text{ K}}$$

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**5.21.** Benzene and toluene form nearly ideal solutions. If, at 300 K,  $P^*$  (toluene) = 3.572 kPa and  $P^*$  (benzene) = 9.657 kPa, compute the vapor pressure of a solution containing 0.60 mol fraction of toluene. What is the mole fraction of toluene in the vapor over this liquid?

**Solution:**

Given:  $x_{\text{toluene}} = 0.60$ ,  $x_{\text{benzene}} = 0.40$ ,  $T = 300$  K,  $P_{\text{toluene}}^* = 3.572$  kPa,  $P_{\text{benzene}}^* = 9.657$  kPa

Required:  $P_{\text{total}}$ ,  $x_{\text{toluene}}^{\text{vapor}}$

The total pressure is given by the sum of partial pressures of each of the components in a mixture:

$$P_{\text{total}} = P_{\text{toluene}} + P_{\text{benzene}}$$

Raoult's Law is given by Eq. 5.26, and can be used to solve for  $P_{\text{total}}$ .

$$P_1 = x_1 P_1^*; \quad P_2 = x_2 P_2^*$$

$$P_{\text{toluene}} = 0.60(3.572 \text{ kPa})$$

$$P_{\text{toluene}} = 2.1432 \text{ kPa}$$

$$P_{\text{benzene}} = 0.40(9.657 \text{ kPa})$$

$$P_{\text{benzene}} = 3.8628 \text{ kPa}$$

$$P_{\text{total}} = 2.1432 \text{ kPa} + 3.8628 \text{ kPa}$$

$$\boxed{P_{\text{total}} = 6.006 \text{ kPa}}$$

The mole fraction of toluene in the vapor over the liquid is given by the partial pressure of toluene divided by the total pressure of the vapor.

$$x_{\text{toluene}}^{\text{vapor}} = \frac{P_{\text{toluene}}}{P_{\text{total}}}$$

$$x_{\text{toluene}}^{\text{vapor}} = \frac{2.1432 \text{ kPa}}{6.006 \text{ kPa}}$$

$$x_{\text{toluene}}^{\text{vapor}} = 0.356843$$

$$x_{\text{toluene}}^{\text{vapor}} = 0.3568$$

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**5.22.** Often it is important to express one unit of concentration in terms of another. Derive a general expression to find the mole fraction  $x_2$  in a two-component system where the molality is given as  $m_2$ .

**Solution:**

The molality,  $m_2$ , is the amount of solute divided by the mass of solvent. If  $W_1$  is the mass of solvent, the solution contains  $m_2 W_1$  moles of solute and  $\frac{W_1}{M_1}$  moles of solvent. The mole fraction is thus:

$$x_2 = \frac{m_2 W_1}{\frac{W_1}{M_1} + m_2 W_1}$$

$$x_2 = \frac{\cancel{m_2 W_1}}{\cancel{W_1} \left( \frac{1}{M_1} + m_2 \right)}$$

$$x_2 = \frac{m_2}{\left( \frac{1}{M_1} + m_2 \right)}$$

Multiplying through by  $\frac{M_1}{M_1}$  gives,

$$x_2 = \frac{m_2 M_1}{(1 + M_1 m_2)}$$

Dividing each term by its SI unit yields;

$$x_2 = \frac{\left( \frac{m_2}{\text{mol kg}^{-1}} \right) \left( \frac{M_1}{\text{kg mol}^{-1}} \right)}{1 + \left( \frac{m_2}{\text{mol kg}^{-1}} \right) \left( \frac{M_1}{\text{kg mol}^{-1}} \right)}$$

However, the customary unit for molar mass  $M_1$ , is  $\text{g mol}^{-1}$ , therefore we obtain,



$$x_2 = \frac{\left(\frac{m_2}{\text{mol kg}^{-1}}\right)\left(\frac{M_1}{1000 \text{ g mol}^{-1}}\right)}{1 + \left(\frac{m_2}{\text{mol kg}^{-1}}\right)\left(\frac{M_1}{1000 \text{ g mol}^{-1}}\right)}$$

Multiplying through by  $\frac{1000}{1000}$  gives,

$$x_2 = \frac{\left(\frac{m_2}{\text{mol kg}^{-1}}\right)\left(\frac{M_1}{\text{g mol}^{-1}}\right)}{1000 + \left(\frac{m_2}{\text{mol kg}^{-1}}\right)\left(\frac{M_1}{\text{g mol}^{-1}}\right)}$$

For sufficiently dilute solutions, the expression approximates to the following:

$$x_2 \approx \frac{\left(\frac{m_2}{\text{mol kg}^{-1}}\right)\left(\frac{M_1}{\text{g mol}^{-1}}\right)}{1000}$$

Therefore the general expression for mole fraction,  $x_2$ , in a two-component system is:

$$x_2 = \frac{\left(\frac{m_2}{\text{mol kg}^{-1}}\right)\left(\frac{M_1}{\text{g mol}^{-1}}\right)}{1000}$$

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- 5.23.** Assuming that commercially available automotive antifreeze is pure ethylene glycol (it actually also contains relatively small amounts of added rust inhibitors and a fluorescent dye that helps to differentiate a radiator leak from condensation from the air conditioner), in what ratio *by volume* will antifreeze and water have to be mixed in order to have a solution that freezes at  $-20.0\text{ }^{\circ}\text{C}$ ? What will be the boiling point of this solution at 1 atm pressure? (MW =  $62.02\text{ g mol}^{-1}$ , density =  $1.1088\text{ g cm}^{-3}$ .)

**Solution:**

Given:  $\Delta_{\text{fus}}T = 20.0\text{ }^{\circ}\text{C} = 20.0\text{ K}$ ,  $M_2 = 62.02\text{ g mol}^{-1}$ ,  $\rho = 1.1088\text{ g cm}^{-3}$ ,  $P = 1\text{ atm}$

Required:  $V$  ratio,  $T$

To solve for the volume ratio, we must first determine the mass of antifreeze present by using Eq. 5.122:

$$M_2 = \frac{K_f W_2}{\Delta_{\text{fus}} T W_1}$$

Rearranging for  $W_2$  gives,

$$W_2 = \frac{M_2 \Delta_{\text{fus}} T W_1}{K_f}$$

Where  $W_1$  is 1.00 kg since we are solving for the ratio and  $K_f$  is the freezing point depression constant for water given in Table 5.2. Given that,

$\Delta_{\text{fus}}T = 20.0\text{ }^{\circ}\text{C} = 20.0\text{ K}$ ,  $M_2 = 62.02\text{ g mol}^{-1}$ ,  $\rho = 1.1088\text{ g cm}^{-3}$ ,  $P = 1\text{ atm}$

$$W_2 = \frac{(0.06202\text{ kg mol}^{-1})(20.0\text{ K})(1.00\text{ kg})}{1.86\text{ K kg mol}^{-1}}$$

$$W_2 = 0.666\ 881\ 720\ 4\text{ kg}$$

Using the definition of density, we can convert the mass of antifreeze into the volume of antifreeze.

$$\rho = 1.1088 \text{ g cm}^{-3} = 1.1088 \text{ kg dm}^{-3}$$

$$\rho = \frac{W_2}{V}$$

$$V = \frac{W_2}{\rho}$$

$$V = \frac{0.666\,881\,720\,4 \text{ kg}}{1.1088 \text{ kg dm}^{-3}}$$

$$V = 0.601\,444\,553\,1 \text{ dm}^3$$

$$\boxed{V = 0.601 \text{ dm}^3}$$

Therefore the volume ratio is 0.601 dm<sup>3</sup> antifreeze to 1.0 dm<sup>3</sup> of water. (Or approximately 3:5)

The elevation of boiling point for this solution is given by Eq. 5.126 which states that:

$$\Delta_{\text{vap}} T = K_b m_2$$

Where  $\Delta_{\text{vap}} T = T - T_b^*$  and  $K_b$  is the boiling point depression constant given in Table 5.4. Solving for  $T$ , we obtain,

$$m_2 = \frac{W_2}{M_2}$$

$$T - T_b^* = \left(0.51 \text{ K kg mol}^{-1}\right) \frac{0.666\,881\,720\,4 \text{ kg}}{(0.06202 \text{ kg mol}^{-1})}$$

$$T - T_b^* = 5.483\,870\,968 \text{ K}$$

$$T = 5.483\,870\,968 \text{ K} + T_b^*$$

$$T_b^* = 373.15 \text{ K} \text{ note that this is typically the boiling point of water!}$$

$$T = 5.483\,870\,968\text{ K} + 373.15\text{ K}$$

$$T = 378.633\,870\,968\text{ K}$$

$$T = 378.6\text{ K}$$

This means the solution will boil at 378.6 K.

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**5.24.** The familiar term *molarity* is now discouraged by IUPAC because of the danger of confusion with molality. In its place, *concentration* is defined as the amount of substance 2,  $n_2$ , dissolved in unit volume of solution. Derive a general relation to find  $x_2$  from the concentration  $c_2$ . Let the solution density be  $\rho$ .

**Solution:**

Let component 1 be the solvent and component 2 be the solute in the solution. The concentration,  $c_2$ , is the number of moles of solute divided by the volume of the solution.

$$c_2 = \frac{n_2}{V}$$

From this expression, the amount in moles of solute is,

$$n_2 = Vc_2$$

The mass of the solute is given by  $m = nM$ , hence,

$$m_2 = Vc_2M_2$$

Density is given by  $\rho = \frac{m}{V}$ , therefore the total mass of the solution is given by:

$$m = V\rho$$

The mass of the solvent is then given by the difference in mass of solution and solute,

$$m_1 = V\rho - Vc_2M_2$$

The amount in moles of solvent can then be found according to the following expression.

$$n_1 = \frac{m_1}{M_1} = \frac{V\rho - Vc_2M_2}{M_1}$$

The mole fraction of the solute is the number of moles of the solute divided by the total number of moles present in the solution.

$$x_2 = \frac{Vc_2}{\frac{V\rho - Vc_2M_2}{M_1} + Vc_2}$$

$$x_2 = \frac{\cancel{V}c_2}{\cancel{V}\left(\frac{\rho - c_2M_2}{M_1} + c_2\right)}$$

$$x_2 = \frac{c_2}{\left(\frac{\rho - c_2M_2 + c_2M_1}{M_1}\right)}$$

Multiplying through by  $\frac{M_1}{M_1}$  yields the following;

$$x_2 = \frac{c_2M_1}{\rho + c_2(M_1 - M_2)}$$

Dividing each term by its SI unit gives:

$$x_2 = \frac{\left(\frac{c_2}{\text{mol m}^{-3}}\right)\left(\frac{M_1}{\text{kg mol}^{-1}}\right)}{\left(\frac{\rho}{\text{kg m}^{-3}}\right) + \left(\frac{c_2}{\text{mol m}^{-3}}\right)\left(\frac{M_1}{\text{kg mol}^{-1}} - \frac{M_2}{\text{kg mol}^{-1}}\right)}$$

However, the customary units are, for concentration  $c_2$ , is  $\text{mol dm}^{-3}$ , for molar mass  $M_1$ , is  $\text{g mol}^{-1}$ , for density  $\rho$ , is  $\text{kg dm}^{-3} \equiv \text{g cm}^{-3}$  therefore we obtain,

$$x_2 = \frac{\left(\frac{1000 c_2}{\text{mol dm}^{-3}}\right)\left(\frac{M_1}{1000 \text{ g mol}^{-1}}\right)}{\left(\frac{1000 \rho}{\text{g cm}^{-3}}\right) + \left(\frac{1000 c_2}{\text{mol dm}^{-3}}\right)\left(\frac{M_1}{1000 \text{ g mol}^{-1}} - \frac{M_2}{1000 \text{ g mol}^{-1}}\right)}$$

Further simplification gives,

$$x_2 = \frac{\left(\frac{c_2}{\text{mol dm}^{-3}}\right)\left(\frac{M_1}{\text{g mol}^{-1}}\right)}{\left(\frac{1000 \rho}{\text{g cm}^{-3}}\right) + \left(\frac{c_2}{\text{mol dm}^{-3}}\right)\left(\frac{M_1}{\text{g mol}^{-1}} - \frac{M_2}{\text{g mol}^{-1}}\right)}$$

For sufficiently dilute solutions, the density of the solution is approximately that of the pure solvent,  $\rho_1$ , and the expression approximates to:

$$x_2 \approx \frac{\left(\frac{c_2}{\text{mol dm}^{-3}}\right)\left(\frac{M_1}{\text{g mol}^{-1}}\right)}{\left(\frac{1000 \rho_1}{\text{g cm}^{-3}}\right)}$$

Therefore the general expression for mole fraction,  $x_2$ , in solution is:

$$x_2 = \frac{\left(\frac{c_2}{\text{mol dm}^{-3}}\right)\left(\frac{M_1}{\text{g mol}^{-1}}\right)}{\left(\frac{1000 \rho_1}{\text{g cm}^{-3}}\right)}$$

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**5.25.** Show that if a solute follows Henry's law in the form of  $P_2 = k'x_2$ , then the solvent must follow Raoult's law. (*Hint:* The use of the Gibbs-Duhem equation might prove useful.)

**Solution:**

Henry's law is given by Eq. 5.27 as  $P_1 = k'x_2$ , or  $P_2 = k''c_2$  and Raoult's law is given by,

Eq. 5.26 as  $P_1 = x_1P_1^*$ ;  $P_2 = x_2P_2^*$ .

It is found that in the limit of infinite dilution most liquid solvents obey Raoult's law but that under the same conditions the solute obeys Henry's law.

Eq. 5.101,  $\mu_{i,id} = \mu_i^* + RT \ln x_i$

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**5.26.** A 1.0 *m* solution of NaCl in water produces a freezing point depression of approximately 3.7 K. How can we account for this observation?

**Solution:**

Given:  $c = 1.0 \text{ M}$ ,  $\Delta_{\text{fus}}T = 3.7 \text{ K}$

Required: account for the observation.

The freezing point depression is given by Eq. 5.121, where  $K_f$  is the freezing point depression constant for water provided by Table 5.2.

$$\Delta_{\text{fus}}T = K_f m_2$$

$$\Delta_{\text{fus}}T = (1.86 \text{ K } \cancel{\text{kg}} \cancel{\text{mol}^{-1}})(1.0 \cancel{\text{mol}} \cancel{\text{kg}^{-1}})$$

$$\Delta_{\text{fus}}T = 1.86 \text{ K}$$

However, this is not what is observed.

Colligative properties are, to a large extent, determined by the number of particles in solution, rather than the actual identity of the species. Since NaCl completely ionizes in solution, the resulting solution contains 2.0 moles of particles. Therefore we can calculate the temperature change using;

$$\Delta_{\text{fus}}T = (1.86 \text{ K } \cancel{\text{kg}} \cancel{\text{mol}^{-1}})(2.0 \cancel{\text{mol}} \cancel{\text{kg}^{-1}})$$

$$\Delta_{\text{fus}}T = 3.72 \text{ K} \approx 3.7 \text{ K}$$

The ionization of NaCl accounts for the observed temperature change.

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**5.27.** Derive a general expression to relate the molality  $m$  to concentration  $c_2$ .

**Solution:**

Let component 1 be the solvent and component 2 be the solute in the solution. The molality,  $m_2$ , is the amount of solute divided by the mass of solvent. Using what we have done in problem 5.24, we can say that;

$$n_{\text{solute}} = Vc_2 \quad \text{and} \quad m_{\text{solvent}} = V\rho - Vc_2M_2$$

Therefore, molality can be expressed as,

$$m_2 = \frac{Vc_2}{V\rho - Vc_2M_2}$$

$$m_2 = \frac{c_2}{\rho - c_2M_2}$$

Rearranging the above, we can write concentration in terms of molality.

$$m_2(\rho - c_2M_2) = c_2$$

$$\rho m_2 - c_2m_2M_2 = c_2$$

$$\rho m_2 = c_2 + c_2m_2M_2$$

$$\rho m_2 = c_2(1 + m_2M_2)$$

$$c_2 = \frac{\rho m_2}{(1 + m_2M_2)}$$

Dividing each term by its SI unit yields the following:

$$\left( \frac{c_2}{\text{mol m}^{-3}} \right) = \frac{\left( \frac{\rho}{\text{kg m}^{-3}} \right) \left( \frac{m_2}{\text{mol kg}^{-1}} \right)}{\left( 1 + \left( \frac{m_2}{\text{mol kg}^{-1}} \right) \left( \frac{M_2}{\text{kg mol}^{-1}} \right) \right)}$$

However, the customary units are, for concentration  $c_2$ , is  $\text{mol dm}^{-3}$ , for molar mass  $M_1$ , is  $\text{g mol}^{-1}$ , for density  $\rho$ , is  $\text{kg dm}^{-3} \equiv \text{g cm}^{-3}$  therefore we obtain,

$$\left( \frac{\cancel{1000} c_2}{\text{mol dm}^{-3}} \right) = \frac{\left( \frac{\cancel{1000} \rho}{\text{g cm}^{-3}} \right) \left( \frac{m_2}{\text{mol kg}^{-1}} \right)}{\left( 1 + \left( \frac{m_2}{\text{mol kg}^{-1}} \right) \left( \frac{M_2}{1000 \text{ g mol}^{-1}} \right) \right)}$$

Multiplying through by  $\frac{1000}{1000}$  gives,

$$\left( \frac{c_2}{\text{mol dm}^{-3}} \right) = \frac{1000 \left( \frac{\rho}{\text{g cm}^{-3}} \right) \left( \frac{m_2}{\text{mol kg}^{-1}} \right)}{1000 + \left( \frac{m_2}{\text{mol kg}^{-1}} \right) \left( \frac{M_2}{\text{g mol}^{-1}} \right)}$$

For sufficiently dilute solutions, the expression approximates to:

$$\frac{c_2}{\text{mol dm}^{-3}} \approx \frac{\cancel{1000} \left( \frac{\rho}{\text{g cm}^{-3}} \right) \left( \frac{m_2}{\text{mol kg}^{-1}} \right)}{\cancel{1000}}$$

Therefore the general expression for concentration in terms of molality is given by;

$$\boxed{\frac{c_2}{\text{mol dm}^{-3}} = \left( \frac{\rho}{\text{g cm}^{-3}} \right) \left( \frac{m_2}{\text{mol kg}^{-1}} \right)}$$

Where  $\rho_1$  is the density of the solvent. For aqueous solutions  $\rho_1 \approx 1 \text{ g cm}^{-3}$ , and therefore the numerical values of concentration and the molality, in the above units, are very similar.

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**5.28.** An amalgam of 1.152 g of a metal dissolved in 100.0 g of mercury is heated to boiling. The partial pressure of mercury vapor over the boiling mixture is 754.1 Torr and the total pressure is 768.8 Torr. Find the atomic weight of the metal and, therefore, its identity.

**Solution:**

Given:  $m_{\text{metal}} = 1.152 \text{ g}$ ,  $m_{\text{Hg}} = 100.0 \text{ g}$ ,  $P_{\text{Hg}} = 754.1 \text{ Torr}$ ,  $P_{\text{Hg}}^* = 768.8 \text{ Torr}$

Required:  $M_{\text{metal}}$

Raoult's Law is given by Eq. 5.26. It can be rearranged so that we can solve for  $x_{\text{Hg}}$  and hence  $x_{\text{metal}}$  since  $x_{\text{metal}} + x_{\text{Hg}} = 1$ .

$$P_1 = x_1 P_1^*$$

$$x_1 = \frac{P_1}{P_1^*}$$

$$x_{\text{Hg}} = \frac{P_{\text{Hg}}}{P_{\text{Hg}}^*}$$

$$x_{\text{metal}} = 1 - x_{\text{Hg}}$$

$$x_{\text{metal}} = 1 - \frac{754.1 \cancel{\text{ Torr}}}{768.8 \cancel{\text{ Torr}}}$$

$$x_{\text{metal}} = 0.0191207076$$

The mole fraction is given by,

$$x_{\text{metal}} = \frac{n_{\text{metal}}}{n_{\text{metal}} + n_{\text{Hg}}}$$

Rearranging the above in order to isolate for the number of moles for the metal gives,

$$x_{\text{metal}} (n_{\text{metal}} + n_{\text{Hg}}) = n_{\text{metal}}$$

$$n_{\text{metal}} x_{\text{metal}} + n_{\text{Hg}} x_{\text{metal}} = n_{\text{metal}}$$

$$n_{\text{metal}} x_{\text{metal}} - n_{\text{metal}} = -n_{\text{Hg}} x_{\text{metal}}$$

$$n_{\text{metal}} (x_{\text{metal}} - 1) = -n_{\text{Hg}} x_{\text{metal}}$$

$$n_{\text{metal}} = \frac{-n_{\text{Hg}} x_{\text{metal}}}{(x_{\text{metal}} - 1)}$$

$$n_{\text{metal}} = \frac{n_{\text{Hg}} x_{\text{metal}}}{(1 - x_{\text{metal}})}, \text{ where } n = \frac{m}{M}$$

Once we have determined this value, we can easily find the molar mass for the metal.

$$n_{\text{metal}} = \frac{x_{\text{metal}}}{(1 - x_{\text{metal}})} \frac{m_{\text{Hg}}}{M_{\text{Hg}}}$$

$$n_{\text{metal}} = \frac{0.019\,120\,707\,6}{(1 - 0.019\,120\,707\,6)} \left( \frac{100.0 \cancel{\text{g}}}{200.59 \cancel{\text{g}} \text{ mol}^{-1}} \right)$$

$$n_{\text{metal}} = 0.009\,718\,049\,7 \text{ mol}$$

$$\frac{m_{\text{metal}}}{M_{\text{metal}}} = 0.009\,718\,049\,7 \text{ mol}$$

$$M_{\text{metal}} = \frac{1.152 \text{ g}}{0.009\,718\,049\,7 \text{ mol}}$$

$$M_{\text{metal}} = 118.542\,303\,9 \text{ g mol}^{-1}$$

$$\boxed{M_{\text{metal}} = 118.54 \text{ g mol}^{-1}}$$

The molar mass is  $118.54 \text{ g mol}^{-1}$  which is approximately the same as the molar mass of tin,  $118.710 \text{ g mol}^{-1}$ , therefore we can assume that the identity of the metal is tin.

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**5.29.** The volume of a solution of NaCl in water is given by the expression

$$V/\text{cm}^3 = 1002.874 + 17.8213 m + 0.873\,91 m^2 - 0.047\,225 m^3$$

where  $m$  is the molality. Assume that  $m \propto n_{\text{NaCl}}$  and that  $n_{\text{H}_2\text{O}} = 55.508$  mol, where  $V_{\text{H}_2\text{O}}^* = 18.068$  cm<sup>3</sup>. Derive an analytical expression for the partial molar volume of H<sub>2</sub>O in the solution.

**Solution:**

The partial derivative for the molar volume of a solution is given by Eq. 5.31 which states that;

$$V_1 \equiv \left( \frac{\partial V}{\partial n_1} \right)_{T, P, n_2, n_3, \dots}$$

When can applying this general equation to the expression given in the problem which gives;

$$V_{\text{NaCl}} = \left( \frac{\partial V}{\partial n_{\text{NaCl}}} \right)_{n_{\text{H}_2\text{O}}} = \left( \frac{\partial V}{\partial m} \right)$$

$$V_{\text{NaCl}} / \text{cm}^3 = 17.8213 + 1.747\,82 m - 0.141\,675 m^2$$

We can now use Eq. 5.37, the Gibbs-Duhem equation, to obtain an expression for  $dV_{\text{H}_2\text{O}}$ .

$$dV_1 = - \frac{n_2}{n_1} dV_2$$

$$dV_{\text{H}_2\text{O}} = - \frac{n_{\text{NaCl}}}{n_{\text{H}_2\text{O}}} dV_{\text{NaCl}}$$

$$\frac{dV_{\text{NaCl}}}{dm} = 1.747\,82 - 0.283\,35 m$$

$$dV_{\text{H}_2\text{O}} = - \frac{n_{\text{NaCl}}}{n_{\text{H}_2\text{O}}} (1.747\,82 - 0.283\,35 m)$$

We are working under the assumption that ;  $m \propto n_{\text{NaCl}}$  and since  $n_{\text{H}_2\text{O}} = 55.508$  mol. It is now possible to integrate the above expression in order to solve for  $V_{\text{H}_2\text{O}}$ , the partial molar volume of H<sub>2</sub>O.

$$dV_{\text{H}_2\text{O}} = -\frac{m}{55.508 \text{ mol}}(1.74782 - 0.28335 m)$$

$$dV_{\text{H}_2\text{O}} = -\frac{1}{55.508 \text{ mol}}(1.74782 m - 0.28335 m^2)$$

$$\int dV_{\text{H}_2\text{O}} = \int -\frac{1}{55.508 \text{ mol}}(1.74782 m - 0.28335 m^2) dm$$

$$V_{\text{H}_2\text{O}} - V_{\text{H}_2\text{O}}^* = -\frac{1}{55.508 \text{ mol}} \int (1.74782 m - 0.28335 m^2) dm$$

$$V_{\text{H}_2\text{O}} - V_{\text{H}_2\text{O}}^* = -\frac{1}{55.508 \text{ mol}}(0.87391 m^2 - 0.09445 m^3)$$

$$V_{\text{H}_2\text{O}} = -\frac{1}{55.508 \text{ mol}}(0.87391 m^2 - 0.09445 m^3) + V_{\text{H}_2\text{O}}^*$$

$$V_{\text{H}_2\text{O}}/\text{cm}^3 \text{ mol}^{-1} = 18.068 \text{ cm}^3 - \frac{1}{55.508 \text{ mol}}(0.87391 m^2 - 0.09445 m^3)$$

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**5.30.** The partial molar volume of component 2 in a solution may be written as

$$\begin{aligned} V_2 &= \left( \frac{\partial V}{\partial n_2} \right)_{n_1} \\ &= \frac{M_2}{\rho} - (M_1 n_1 + M_2 n_2) \frac{1}{\rho^2} \left( \frac{\partial \rho}{\partial n_2} \right)_{n_1} \end{aligned}$$

where  $n_1$  and  $M_1$  are amount and molar mass of component 1 and  $n_2$  and  $M_2$  represent the same quantities for component 2. The density is  $\rho$ . Rewrite the expression in terms of the mole fractions  $x_1$  and  $x_2$ .

**Solution:**

Recall that the mole fraction for a species is given by ;

$$x_2 = \frac{n_2}{n_1 + n_2}, \quad x_1 = \frac{n_1}{n_1 + n_2}$$

Therefore we must first develop an expression for  $\left( \frac{\partial \rho}{\partial n_2} \right)_{n_1}$  using this definition.

$$\left( \frac{\partial x_2}{\partial n_2} \right)_{n_1} = \frac{n_1 + n_2 - 1(n_2)}{(n_1 + n_2)^2}$$

$$\left( \frac{\partial x_2}{\partial n_2} \right)_{n_1} = \frac{n_1}{(n_1 + n_2)^2}$$

By using Euler's Chain Rule outlined in Appendix C we can formulate the appropriate expression.

$$\left( \frac{\partial \rho}{\partial n_2} \right)_{n_1} = \frac{d\rho}{dx_2} \left( \frac{\partial x_2}{\partial n_2} \right)_{n_1}$$

$$\left( \frac{\partial \rho}{\partial n_2} \right)_{n_1} = \frac{n_1}{(n_1 + n_2)^2} \frac{d\rho}{dx_2}$$



We can now substitute the above into the expression for  $V_2$  given in the problem to produce,

$$V_2 = \frac{M_2}{\rho} - (M_1 n_1 + M_2 n_2) \frac{1}{\rho^2} \left( \frac{n_1}{(n_1 + n_2)^2} \frac{d\rho}{dx_2} \right)$$

Since we know that  $x_2 = \frac{n_2}{n_1 + n_2}$ ,  $x_1 = \frac{n_1}{n_1 + n_2}$ , it follows that the expression becomes,

$$V_2 = \frac{M_2}{\rho} - (M_1 n_1 + M_2 n_2) \frac{1}{\rho^2} \left( \frac{1}{(n_1 + n_2)} \frac{n_1}{(n_1 + n_2)} \frac{d\rho}{dx_2} \right)$$

$$V_2 = \frac{M_2}{\rho} - \left( \frac{M_1 n_1}{(n_1 + n_2)} + \frac{M_2 n_2}{(n_1 + n_2)} \right) \frac{1}{\rho^2} \left( x_1 \frac{d\rho}{dx_2} \right)$$

$$\boxed{V_2 = \frac{M_2}{\rho} - (M_1 x_1 + M_2 x_2) \frac{x_1}{\rho^2} \left( \frac{d\rho}{dx_2} \right)}$$

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**5.31.** Mikhail and Kimel, *J. Chem. Eng. Data*, 6, 533(1961), give the density of a water-methanol solution in  $\text{g cm}^{-3}$  at 298 K related to the mole fraction  $x_2$  of the methanol through the equation

$$\rho/\text{g cm}^{-3} = 0.9971 - 0.28930x_2 + 0.29907x_2^2 \\ - 0.60876x_2^3 + 0.59438x_2^4 - 0.20581x_2^5$$

Using the equation developed in Problem 5.30, calculate  $V_2$  at 298 K when  $x_2 = 0.100$ .

**Solution:**

Given:  $T = 298 \text{ K}$ ,  $x_2 = 0.100$

Required:  $V_2$

We can make use of the equation developed for  $V_2$  in the previous problem (5.30).

$$V_2 = \frac{M_2}{\rho} - (M_1x_1 + M_2x_2) \frac{x_1}{\rho^2} \left( \frac{d\rho}{dx_2} \right)$$

In this particular problem,  $M_1$  is the molar mass of water,  $M_2$  is the molar mass of methanol, and  $x_1$  is the mole fraction of water.

$$x_1 = 1 - x_2$$

$$x_1 = 1 - 0.100$$

$$x_1 = 0.900$$

$$M_1 = 2(1.00794 \text{ g mol}^{-1}) + 15.9994 \text{ g mol}^{-1}$$

$$M_1 = 18.01528 \text{ g mol}^{-1}$$

$$M_2 = 12.011 \text{ g mol}^{-1} + 4(1.00794 \text{ g mol}^{-1}) + 15.9994 \text{ g mol}^{-1}$$

$$M_2 = 32.04216 \text{ g mol}^{-1}$$

Solving for  $\rho$ , where  $x_2 = 0.100$  gives,

$$\rho = 0.9971 - 0.28930(0.100) + 0.29907(0.100)^2 - 0.60876(0.100)^3 + 0.59438(0.100)^4 - 0.20581(0.100)^5$$

$$\rho = 0.970\,609\,319\,9 \text{ g cm}^{-3}$$

$$\rho^2 = 0.942\,082\,451\,9 \text{ g}^2 \text{ cm}^{-6}$$

$\rho$  with respect to  $x_2$ ,

$$\frac{d\rho}{dx_2} = -0.289\,30 + 0.598\,14 x_2 - 1.826\,28 x_2^2 + 2.377\,52 x_2^3 - 1.029\,05 x_2^4$$

$$\frac{d\rho}{dx_2} = -0.289\,30 + 0.598\,14(0.100) - 1.826\,28(0.100)^2 + 2.377\,52(0.100)^3 - 1.029\,05(0.100)^4$$

$$\frac{d\rho}{dx_2} = -0.245\,474\,185 \text{ g cm}^{-3}$$

We can now take the derivative of

Now that we have found all of the required values, we can make the appropriate substitutions into the expression we found for  $V_2$  to obtain,

$$V_2 = \frac{32.042\,16 \cancel{\text{g}} \text{ mol}^{-1}}{0.970\,609\,319\,9 \cancel{\text{g}} \text{ cm}^{-3}} - \left( (18.015\,28 \cancel{\text{g}} \text{ mol}^{-1})(0.900) + (32.042\,16 \cancel{\text{g}} \text{ mol}^{-1})(0.100) \right)$$

$$\times \frac{0.900}{0.942\,082\,451\,9 \cancel{\text{g}}^2 \text{ cm}^{-6}} (-0.245\,474\,185 \cancel{\text{g}} \text{ cm}^{-3})$$

$$V_2 = 37.566\,104\,68 \cancel{\text{cm}^3} \text{ mol}^{-1} \times 10^{-3} \frac{\text{dm}^3}{\cancel{\text{cm}^3}}$$

$$V_2 = 0.037\,566\,104\,68 \text{ dm}^3 \text{ mol}^{-1}$$

$$\boxed{V_2 = 3.76 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}}$$

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**5.32.** Beckmann and Faust [*Z. Physik. Chemie*, 89, 235(1915)] found that a solution of chloroform in acetone in which the mole fraction of the latter is 0.713 has a total vapor pressure of 220.5 Torr at 28.15 °C. The mole fraction of acetone in the vapor is 0.818. The vapor pressure of pure chloroform at this temperature is 221.8 Torr. Assuming that the vapor behaves ideally, calculate the activity and the activity coefficient of chloroform.

**Solution:**

Given: in solution,  $x_{\text{acetone}} = 0.713$ ,  $P_{\text{total}} = 220.5 \text{ Torr}$ ,  $T = 28.15 \text{ °C} = 301.3 \text{ K}$ ,

in vapor phase,  $x_{\text{acetone}} = 0.818$ ,  $P_{\text{chloroform}}^* = 221.8 \text{ Torr}$

Required:  $a_{\text{chloroform}}$ ,  $f_{\text{chloroform}}$

This problem makes use of Raoult's Law which defines the chemical potential for a pure component  $i$  in terms of a dimensionless activity,  $a_i$ . The activity is given by Eq. 5.75:

$$a_i = \frac{f_i}{f_i^0} = \frac{P_i}{P_i^*}$$

Therefore the activity of chloroform is given by,  $a_{\text{chloroform}} = \frac{P_{\text{chloroform}}}{P_{\text{chloroform}}^*}$

To solve for  $P_{\text{chloroform}}$  we may use Dalton's Law of Partial Pressures with the mole fraction of pure chloroform in the vapor phase. This will yield the following:

$$x_{\text{chloroform}} = 1 - x_{\text{acetone}}$$

$$P_{\text{chloroform}} = (1 - 0.818) 220.5 \text{ Torr}$$

$$P_{\text{chloroform}} = 40.131 \text{ Torr}$$

$$a_{\text{chloroform}} = \frac{40.131 \cancel{\text{ Torr}}}{221.8 \cancel{\text{ Torr}}}$$

$$a_{\text{chloroform}} = 0.1809332732$$

$$\boxed{a_{\text{chloroform}} = 0.181}$$

The usual procedure in dealing with solvent species (as we have already seen) is to use the mole fraction. In chapter 4 (specifically section 4.3) we defined the Gibbs Free Energy by Eq. 4.48 which states that:

$$G = G^{\circ} + RT \ln(x_1 f_1)$$

Since we know that when using Raoult's Law  $\mu_i = \frac{G_i}{n_i}$  which subsequently allows us to write;

$$\mu_i = \mu_i^* + RT \ln f_i^u = \mu_i^* + RT \ln a_i$$

With this, we can say that the activity coefficient is given by  $f_i = a_i/x_i$ .

$$f_{\text{chloroform}} = \frac{a_{\text{chloroform}}}{1 - x_{\text{acetone}}}$$

$$f_{\text{chloroform}} = \frac{0.180\,933\,273\,2}{1 - 0.713}$$

$$f_{\text{chloroform}} = 0.630\,429\,523\,4$$

$$\boxed{f_{\text{chloroform}} = 0.630}$$

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**5.33.** When 12.5 g of A, a nonvolatile compound, is dissolved in 520.8 g of ethanol, the vapor pressure of the pure solvent, 56.18 Torr, is reduced to 55.24 Torr. Calculate the molar mass of compound A.

**Solution:**

Given:  $m_A = 12.5 \text{ g}$ ,  $m_{\text{ethanol}} = 520.8 \text{ g}$ ,  $P_{\text{ethanol}}^* = 56.18 \text{ Torr}$ ,  $P_{\text{ethanol}} = 55.24 \text{ Torr}$

Required:  $M_A$

This problem again refers to Raoult's Law (for ideal solutions). The following form of Raoult's Law (Eq. 5.78) is especially useful for solutions of relatively involatile solutes in a volatile solvent.

$$\left(\frac{P_1}{P_1^*}\right) - 1 = x_1 - 1 \text{ or rather } \left(\frac{P_1^* - P_1}{P_1^*}\right) = x_2$$

Eq. 5.78 may be written so that the molar mass of the solute 2 may be determined. For a dilute solution,  $n_2$  may be neglected in the denominator (Eq. 5.79) and we obtain Eq. 5.80;

$$\frac{P_1^* - P_1}{P_1^*} = \frac{n_2}{n_1} = \frac{W_2}{M_2} \cdot \frac{M_1}{W_1}$$

Rearranging the above in order to isolate for  $M_2$  gives,

$$M_2 = W_2 \frac{M_1}{W_1} \frac{P_1^*}{P_1^* - P_1}$$

$$M_1 = 2(12.011 \text{ g mol}^{-1}) + 6(1.00794 \text{ g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_1 = 46.06904 \text{ g mol}^{-1}$$

$$M_A = (12.5 \cancel{\text{ g}}) \frac{46.06904 \text{ g mol}^{-1}}{520.8 \cancel{\text{ g}}} \frac{56.18 \cancel{\text{ Torr}}}{56.18 \cancel{\text{ Torr}} - 55.24 \cancel{\text{ Torr}}}$$

$$M_A = 66.08487625 \text{ g mol}^{-1}$$

$$\boxed{M_A = 66.1 \text{ g mol}^{-1}}$$

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**5.34.** The following data are for mixtures of isopropanol (I) in benzene (B) at 25 °C.

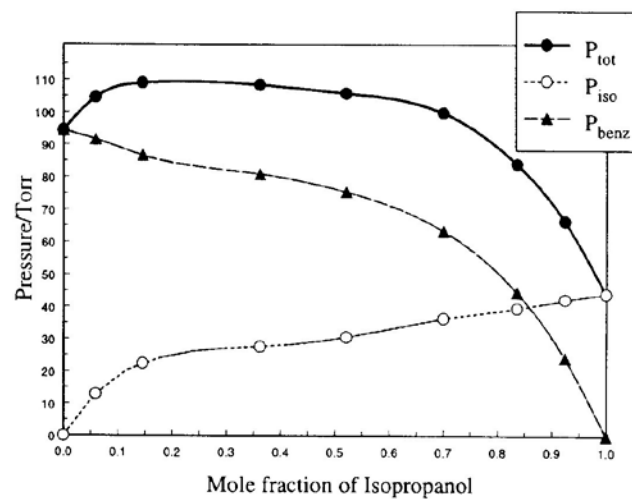
$x_I$	0	0.059	0.146	0.362			
$P_I$ (Torr)	0	12.9	22.4	27.6			
$P_{\text{tot}}$	94.4	104.5	109.0	108.4			
		0.521	0.700	0.836	0.924	1.0	
		30.5	36.4	39.5	42.2	44.0	
		105.8	99.8	84.0	66.4	44.0	

Does this solution exhibit positive or negative deviation from Raoult's law? From a pressure-composition plot, estimate the activities  $a_I$  and  $a_B$  and activity coefficients  $f_I$  and  $f_B$  at  $x_I = 0.20, 0.50$ , and  $0.80$ . [Data from Olsen and Washburn, *J. Phys. Chem.*, 41, 457(1937).]

**Solution:**

Given:

Required:

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**5.35.** The vapor pressure of pure ethylene dibromide is 172 Torr and that of pure propylene dibromide is 128 Torr both at 358 K and 1 atm pressure. If these two components follow Raoult's law, estimate the total vapor pressure in kPa and the vapor composition in equilibrium with a solution that is 0.600 mol fraction propylene dibromide.

**Solution:**

Given:  $P_e^* = 172$  Torr,  $P_p^* = 128$  Torr,  $T = 358$  K,  $P = 1$  atm,  $x_p = 0.600$

Required:  $P_{\text{total}}$ ,  $x_e$ ,  $x_p$  in vapor

The total pressure is given by the sum of partial pressures for each of the components in a mixture.

$$P_{\text{total}} = P_e + P_p$$

Raoult's Law is given by Eq. 5.26, therefore we can use it solve for  $P_{\text{total}}$ .

$$P_1 = x_1 P_1^*; \quad P_2 = x_2 P_2^*$$

$$P_e = 0.400(172 \text{ Torr})$$

$$P_e = 68.8 \text{ Torr}$$

$$P_p = 0.600(128 \text{ Torr})$$

$$P_p = 76.8 \text{ Torr}$$

$$P_{\text{total}} = 68.8 \text{ Torr} + 76.8 \text{ Torr}$$

$$P_{\text{total}} = 145.6 \cancel{\text{ Torr}} \times \frac{101\,325 \text{ Pa}}{760 \cancel{\text{ Torr}}}$$

$$P_{\text{total}} = 19\,411.736\,84 \text{ Pa}$$

$$\boxed{P_{\text{total}} = 19.4 \text{ kPa}}$$

The vapor composition is given by the mole fractions in the vapor over the solution. The mole fraction for a species is given by the partial pressure divided by the total pressure of the vapor.

$$x_e = \frac{P_e}{P_{\text{total}}}$$

$$x_e = \frac{68.8 \text{ Torr}}{145.6 \text{ Torr}}$$

$$x_e = 0.472\ 527\ 472\ 5$$

$$\boxed{x_e = 0.473}$$

$$x_p = \frac{P_p}{P_{\text{total}}}$$

$$x_p = \frac{76.8 \text{ Torr}}{145.6 \text{ Torr}}$$

$$x_p = 0.527\ 472\ 527\ 5$$

$$\boxed{x_p = 0.527}$$

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**5.36.** Calculate Henry's law constant and the vapor pressure of pure liquid A (molar mass =  $89.5 \text{ g mol}^{-1}$ ) and that of 75.0 g of liquid A in solution with 1000 g of liquid B. Liquid B (molar mass =  $185 \text{ g mol}^{-1}$ ) has a pressure in this solution of 430 Torr and the total solution pressure is 520 Torr.

**Solution:**

Given:  $M_A = 89.5 \text{ g mol}^{-1}$ ,  $m_A = 75.0 \text{ g}$ ,  $M_B = 185 \text{ g mol}^{-1}$ ,  $m_B = 1000 \text{ g}$ ,

$$P_B = 430 \text{ Torr}, P_{\text{total}} = 520 \text{ Torr}$$

Required:  $k'$ ,  $P_A$

The total pressure is given by the sum of partial pressures for each of the components in a mixture.

$$P_{\text{total}} = P_A + P_B$$

Solving for  $P_A$  gives,

$$P_A = P_{\text{total}} - P_B$$

$$P_A = 520 \text{ Torr} - 430 \text{ Torr}$$

$$\boxed{P_A = 90 \text{ Torr}}$$

Henry's Law is given by Eq. 5.27 which states that:

$$P_1 = k'x_2$$

To solve for Henry's Law constant, we first need to obtain the mole fraction of species A.

$$x_A = \frac{n_A}{n_A + n_B}$$

$$\text{where } n = \frac{m}{M}$$

$$x_A = \frac{\frac{75.0 \text{ g}}{89.5 \text{ g mol}^{-1}}}{\frac{75.0 \text{ g}}{89.5 \text{ g mol}^{-1}} + \frac{1000 \text{ g}}{185 \text{ g mol}^{-1}}}$$

$$x_A = 0.134\,220\,072\,6$$

We can now rearrange Henry's Law (given above) to isolate for  $k'$  which gives,

$$k' = \frac{P_1}{x_2}$$

$$k' = \frac{90 \text{ Torr}}{0.134\,220\,072\,6}$$

$$k' = 670.540\,540\,3 \text{ Torr}$$

$$\boxed{k' = 671 \text{ Torr}}$$

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**5.37.** Henry's law constants  $k'$  for  $\text{N}_2$  and  $\text{O}_2$  in water at  $20.0^\circ\text{C}$  and 1 atm pressure are  $7.58 \times 10^4$  atm and  $3.88 \times 10^4$  atm, respectively. If the density of water at  $20.0^\circ\text{C}$  is  $0.9982 \text{ g cm}^{-3}$ , calculate (a) the equilibrium mole fraction and (b) the concentration of  $\text{N}_2$  and  $\text{O}_2$  in water exposed to air at  $20.0^\circ\text{C}$  and 1 atm total pressure. Assume in this case that air is 80.0 mol %  $\text{N}_2$  and 20.0 mol %  $\text{O}_2$ .

**Solution:**

Given:  $T = 20.0^\circ\text{C} = 293.15 \text{ K}$ ,  $P = 1 \text{ atm}$ ,  $k'_{\text{N}_2} = 7.58 \times 10^4 \text{ atm}$ ,  $k'_{\text{O}_2} = 3.88 \times 10^4 \text{ atm}$ ,  $\rho = 0.9982 \text{ g cm}^{-3}$ ,  $x_{\text{N}_2} = 0.800$ ,  $x_{\text{O}_2} = 0.200$

Required:

a)  $x_{\text{N}_2}$ ,  $x_{\text{O}_2}$  at equilibrium

b)  $c_{\text{N}_2}$ ,  $c_{\text{O}_2}$

Recall that Henry's Law is given by Eq. 5.27 which states that:

$$P_1 = k'x_2$$

To solve for the mole fraction of a species at equilibrium, we first need to obtain  $P_{\text{N}_2}$  and  $P_{\text{O}_2}$ . The partial pressures,  $P_{\text{N}_2}$  and  $P_{\text{O}_2}$ , are given by the mole fraction multiplied by the total pressure.

$$P_{\text{N}_2} = x_{\text{N}_2} P_{\text{total}}$$

$$P_{\text{N}_2} = (0.800)(1 \text{ atm})$$

$$P_{\text{N}_2} = 0.800 \text{ atm}$$

$$P_{\text{O}_2} = (0.200)(1 \text{ atm})$$

$$P_{\text{O}_2} = 0.200 \text{ atm}$$

Now we can determine the values for  $x_{\text{N}_2}$  and  $x_{\text{O}_2}$  according to:

$$x_{\text{N}_2} = \frac{P_{\text{N}_2}}{k'_{\text{N}_2}}$$

$$x_{\text{N}_2} = \frac{0.800 \text{ atm}}{7.58 \times 10^4 \text{ atm}}$$

$$x_{\text{N}_2} = 1.055\,408\,971 \times 10^{-5}$$

$$\boxed{x_{\text{N}_2} = 1.06 \times 10^{-5}}$$

$$x_{\text{O}_2} = \frac{0.200 \text{ atm}}{3.88 \times 10^4 \text{ atm}}$$

$$x_{\text{O}_2} = 5.154\,639\,175 \times 10^{-6}$$

$$\boxed{x_{\text{O}_2} = 5.15 \times 10^{-6}}$$

We can use 1 mole of water as a reference, and therefore obtain:

$$n_{\text{N}_2} = 1.055\,408\,971 \times 10^{-5} \text{ mol and } n_{\text{O}_2} = 5.154\,639\,175 \times 10^{-6} \text{ mol}$$

By using the density of water, we are able to solve for the concentration.

$$c = \frac{n}{V}$$

$$\rho = \frac{m}{V}$$

$$V = \frac{m}{\rho} = \frac{n_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}}{\rho}$$

$$c = \frac{n\rho}{n_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}}$$

$$M_{\text{H}_2\text{O}} = 2(1.007\,94\text{ g mol}^{-1}) + (15.9994\text{ g mol}^{-1})$$

$$M_{\text{H}_2\text{O}} = 18.015\,28\text{ } \cancel{\text{g}}\text{ mol}^{-1} \times 10^{-3} \frac{\text{kg}}{\cancel{\text{g}}}$$

$$M_{\text{H}_2\text{O}} = 1.801\,528 \times 10^{-2}\text{ kg mol}^{-1}$$

$$c_{\text{N}_2} = \frac{(1.055\,408\,971 \times 10^{-5}\text{ mol})(0.9982\text{ } \cancel{\text{kg}}\text{ dm}^{-3})}{1\text{ } \cancel{\text{mol}} (1.801\,528 \times 10^{-2}\text{ } \cancel{\text{kg}}\text{ } \cancel{\text{mol}^{-1}})}$$

$$c_{\text{N}_2} = 5.847\,864\,895 \times 10^{-4}\text{ mol dm}^{-3}$$

$$\boxed{c_{\text{N}_2} = 5.85 \times 10^{-4}\text{ mol dm}^{-3}}$$

$$c_{\text{O}_2} = \frac{(5.154\,639\,175 \times 10^{-6}\text{ mol})(0.9982\text{ } \cancel{\text{kg}}\text{ dm}^{-3})}{1\text{ } \cancel{\text{mol}} (1.801\,528 \times 10^{-2}\text{ } \cancel{\text{kg}}\text{ } \cancel{\text{mol}^{-1}})}$$

$$c_{\text{O}_2} = 2.856\,109\,272 \times 10^{-4}\text{ mol dm}^{-3}$$

$$\boxed{c_{\text{O}_2} = 2.86 \times 10^{-4}\text{ mol dm}^{-3}}$$

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**5.38.** Methane dissolves in benzene with a Henry's law constant of  $4.27 \times 10^5$  Torr. Calculate methane's molal solubility in benzene at 25 °C if the pressure above benzene is 750 Torr. The vapor pressure of benzene is 94.6 Torr at 25 °C.

**Solution:**

Given:  $T = 25.0^\circ\text{C} = 298.15\text{ K}$ ,  $k' = 4.27 \times 10^5$  Torr,  $P_{\text{benzene}} = 750\text{ Torr}$ ,  $P_{\text{benzene}}^* = 94.6\text{ Torr}$

Required: methane's molal solubility

To solve this problem, we assume that the total vapor pressure of pure benzene is present in the total pressure of 750.0 Torr.

The total pressure is given by the sum of partial pressures for each of the components in a mixture.

$$P_{\text{total}} = P_{\text{methane}} + P_{\text{benzene}}$$

Solving for  $P_{\text{methane}}$  gives,

$$P_{\text{methane}} = P_{\text{total}} - P_{\text{benzene}}$$

$$P_{\text{methane}} = 750\text{ Torr} - 94.6\text{ Torr}$$

$$P_{\text{methane}} = 655.4\text{ Torr}$$

Using Henry's Law, we can obtain the mole fractions of methane and benzene.

$$P_1 = k'x_2$$

$$x_{\text{methane}} = \frac{P_{\text{methane}}}{k'_{\text{methane}}}$$

$$x_{\text{methane}} = \frac{655.4\text{ Torr}}{4.27 \times 10^5\text{ Torr}}$$

$$x_{\text{methane}} = 0.001\,534\,894\,6$$

$$x_{\text{benzene}} = 1 - x_{\text{methane}}$$

$$x_{\text{benzene}} = 0.998\,465\,105\,4$$

The mole fraction is given by the expression,



$$x_{\text{methane}} = \frac{n_{\text{methane}}}{n_{\text{methane}} + n_{\text{benzene}}}$$

$$\text{Where, } n_{\text{benzene}} = \frac{m_{\text{benzene}}}{M_{\text{benzene}}}$$

In 1000 g of benzene,

$$n_{\text{benzene}} = \frac{1000 \text{ g}}{6(1.00794 \text{ g mol}^{-1}) + 6(12.011 \text{ g mol}^{-1})}$$

$$n_{\text{benzene}} = 12.80186149 \text{ mol}$$

Solving for  $n_{\text{methane}}$  gives the molality of methane,

$$x_{\text{methane}} (n_{\text{methane}} + n_{\text{benzene}}) = n_{\text{methane}}$$

$$n_{\text{benzene}} x_{\text{methane}} = n_{\text{methane}} - n_{\text{methane}} x_{\text{methane}}$$

$$n_{\text{benzene}} x_{\text{methane}} = n_{\text{methane}} (1 - x_{\text{methane}})$$

$$n_{\text{methane}} = \frac{n_{\text{benzene}} x_{\text{methane}}}{1 - x_{\text{methane}}}$$

$$n_{\text{methane}} = \frac{(12.80186149 \text{ mol})(0.0015348946)}{0.9984651054}$$

$$n_{\text{methane}} = 0.0196797144 \text{ mol}$$

$$\boxed{\text{molality}_{\text{methane}} = 1.97 \times 10^{-2} \text{ m}}$$

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**5.39.** In a molar mass determination, 18.04 g of the sugar mannitol was dissolved in 100.0 g of water. The vapor pressure of the solution at 298 K was 2.291 kPa, having been lowered by 0.0410 kPa from the value for pure water. Calculate the molar mass of mannitol.

**Solution:**

Given:  $m_{\text{mannitol}} = 18.04 \text{ g}$ ,  $m_{\text{H}_2\text{O}} = 100.0 \text{ g}$ ,  $T = 298 \text{ K}$ ,  $P_1 = 2.291 \text{ kPa}$ ,  $P_1 - P_1^* = 0.0410 \text{ kPa}$

Required:  $M_{\text{mannitol}}$

We can use the expression for lowering the vapor pressure in solution, given by Eq. 5.79 to solve this problem.

$$\frac{P_1^* - P_1}{P_1^*} = \frac{n_2}{n_1 + n_2} = \frac{W_2/M_2}{(W_1/M_1) + (W_2/M_2)}$$

The above expression can then be rearranged to isolate for  $M_2$ ,

$$\frac{P_1^*}{P_1^* - P_1} = \frac{(W_1/M_1) + (W_2/M_2)}{W_2/M_2}$$

$$\frac{P_1^*}{P_1^* - P_1} (W_2/M_2) = (W_1/M_1) + (W_2/M_2)$$

$$(W_2/M_2) \left( \frac{P_1^*}{P_1^* - P_1} - 1 \right) = (W_1/M_1)$$

$$W_2 \left( \frac{P_1^*}{P_1^* - P_1} - 1 \right) = M_2 (W_1/M_1)$$

$$M_2 = \frac{W_2 \left( \frac{P_1^*}{P_1^* - P_1} - 1 \right)}{(W_1/M_1)}$$

$$M_2 = \frac{M_1 W_2 \left( \frac{P_1^*}{P_1^* - P_1} - 1 \right)}{W_1}$$

$$M_{\text{mannitol}} = \frac{M_{\text{H}_2\text{O}} W_{\text{mannitol}} \left( \frac{P_1^*}{P_1^* - P_1} - 1 \right)}{W_{\text{H}_2\text{O}}}$$

$$\text{where, } P_1^* = P_1^* - P_1 + P_1$$

$$M_{\text{H}_2\text{O}} = 2(1.007\,94 \text{ g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_{\text{H}_2\text{O}} = 18.015\,28 \text{ g mol}^{-1}$$

$$M_{\text{mannitol}} = \frac{(18.015\,28 \text{ g mol}^{-1})(18.04 \text{ g}) \left( \frac{0.0410 \text{ kPa} + 2.291 \text{ kPa}}{0.0410 \text{ kPa}} - 1 \right)}{100.0 \text{ g}}$$

$$M_{\text{mannitol}} = 181.601\,228\,5 \text{ g mol}^{-1}$$

$$\boxed{M_{\text{mannitol}} = 181.6 \text{ g mol}^{-1}}$$

The molecular formula for mannitol is  $\text{C}_6\text{H}_8(\text{OH})_6$ , therefore the actual molar mass is found to be:

$$M = 14(1.007\,94\,\text{g mol}^{-1}) + 6(15.9994\,\text{g mol}^{-1}) + 6(12.011\,\text{g mol}^{-1})$$

$$M = 182.173\,56\,\text{g mol}^{-1}$$

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**5.40.** A liquid has a vapor pressure of 40.00 kPa at 298.15 K. When 0.080 kg of an involatile solute is dissolved in 1 mol of the liquid, the new vapor pressure is 26.66 kPa. What is the molar mass of the solute? Assume that the solution is ideal.

**Solution:**

Given:  $P_1^* = 40.00 \text{ kPa}$ ,  $T = 298.15 \text{ K}$ ,  $m_{\text{solute}} = 0.080 \text{ g}$ ,  $n_{\text{solvent}} = 1 \text{ mol}$ ,  $P_1 = 26.66 \text{ kPa}$

Required:  $M_{\text{solute}}$

This problem makes use of Raoult's Law which is given by Eq. 5.26. We can use it solve for  $x_{\text{solute}}$ .

$$P_1 = x_1 P_1^*; \quad P_2 = x_2 P_2^*$$

$$x_1 = \frac{P_1}{P_1^*}$$

$$x_1 = \frac{26.66 \text{ kPa}}{40.00 \text{ kPa}}$$

$$x_1 = 0.6665$$

$$x_{\text{solvent}} = x_1 = 0.6665$$

The mole fraction of the solute is given by:

$$x_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$n_{\text{solute}} x_{\text{solvent}} + n_{\text{solvent}} x_{\text{solvent}} = n_{\text{solvent}}$$

$$n_{\text{solute}} = \frac{n_{\text{solvent}} (1 - x_{\text{solvent}})}{x_{\text{solvent}}}$$

$$n_{\text{solute}} = \frac{1 \text{ mol} (1 - 0.6665)}{0.6665}$$

$$n_{\text{solute}} = 0.500 \, 375 \, 093 \, 8 \text{ mol}$$

Solving for the molar mass of the solute produces the following;

$$n_{\text{solute}} = \frac{m_{\text{solute}}}{M_{\text{solute}}}$$

$$M_{\text{solute}} = \frac{m_{\text{solute}}}{n_{\text{solute}}}$$

$$M_{\text{solute}} = \frac{0.080 \text{ g}}{0.500\,375\,093\,8 \text{ mol}}$$

$$M_{\text{solute}} = 0.159\,880\,06 \text{ g mol}^{-1}$$

$$\boxed{M_{\text{solute}} = 0.160 \text{ g mol}^{-1}}$$

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**5.41.** Components 1 and 2 form an ideal solution. The pressure of pure component 1 is 13.3 kPa at 298 K, and the corresponding vapor pressure of component 2 is approximately zero. If the addition of 1.00 g of component 2 to 10.00 g of component 1 reduces the total vapor pressure to 12.6 kPa, find the ratio of the molar mass of component 2 to that of component 1.

**Solution:**

Given:  $P_1 = 13.3$  kPa,  $P_2 = 0$  kPa,  $T = 298$  K,  $m_1 = 10.00$  g,  $m_2 = 1.00$  g,  $P_{\text{total}} = 12.6$  kPa

Required:  $\frac{M_2}{M_1}$

For a two-component system, we can use the second form of Eq. 5.78 to obtain  $x_2$ ,

$$\frac{P_1^* - P_1}{P_1^*} = x_2$$

$$x_2 = \frac{13.3 \text{ kPa} - 12.6 \text{ kPa}}{13.3 \text{ kPa}}$$

$$x_2 = 0.0526315789$$

We can now use the expression for lowering the vapor pressure in solution, given by Eq. 5.79, to solve this problem.

$$\frac{P_1^* - P_1}{P_1^*} = \frac{n_2}{n_1 + n_2} = \frac{W_2/M_2}{(W_1/M_1) + (W_2/M_2)}$$

The above may be rearranged to isolate for  $\frac{M_2}{M_1}$  which gives,

$$x_2 = \frac{W_2/M_2}{(W_1/M_1) + (W_2/M_2)}$$

$$x_2(W_1/M_1) + x_2(W_2/M_2) = W_2/M_2$$

$$x_2(W_1/M_1) = (W_2/M_2)(1 - x_2)$$

Multiplying through by  $M_2$  we obtain the following:

$$x_2 W_1 \left( \frac{M_2}{M_1} \right) = W_2 (1 - x_2)$$

$$\frac{M_2}{M_1} = \frac{W_2 (1 - x_2)}{W_1 x_2}$$

$$\frac{M_2}{M_1} = \frac{(1.00 \text{ g})(1 - 0.0526315789)}{(10.00 \text{ g})(0.0526315789)}$$

$$\boxed{\frac{M_2}{M_1} = 1.8}$$

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**5.42.** Pure naphthalene has a melting point of 353.35 K. Estimate the purity of a sample of naphthalene in mol %, if its freezing point is 351.85 K ( $K_f = 7.0 \text{ K kg mol}^{-1}$ ).

**Solution:**

Given:  $T_m = 353.35 \text{ K}$ ,  $T_f = 351.85 \text{ K}$ ,  $K_f = 7.0 \text{ K kg mol}^{-1}$

Required: purity of naphthalene

To determine the purity of naphthalene, we first determine the mass of naphthalene present,  $m_2$  from Eq. 5.121.

$$\Delta_{\text{fus}} T = K_f m_2$$

$$m_2 = \frac{\Delta_{\text{fus}} T}{K_f}$$

$$m_2 = \frac{353.35 \text{ K} - 351.85 \text{ K}}{7.0 \text{ K kg mol}^{-1}}$$

$$m_2 = 0.214 \text{ 285 714 3 mol kg}^{-1}$$

The molecular formula for naphthalene is  $\text{C}_{10}\text{H}_8$ , therefore the molar mass found from the periodic table of the elements is:

$$M = 10(12.011 \text{ g mol}^{-1}) + 8(1.007 \text{ 94 g mol}^{-1})$$

$$M = 128.173 \text{ 52 g mol}^{-1}$$

To determine the molar purity, we can use;

$$\text{molar impurity} = \frac{m_2}{m_{\text{total}}} \times 100\%$$

$$\text{molar impurity} = \frac{0.214\,285\,714\,3 \cancel{\text{mol}} \cancel{\text{kg}}^{-1}}{0.214\,285\,714\,3 \cancel{\text{mol}} \cancel{\text{kg}}^{-1} + \left(128.173\,52 \cancel{\text{g}} \cancel{\text{mol}}^{-1} \times 10^{-3} \cancel{\text{kg}} \cancel{\text{g}}^{-1}\right)^{-1}} \times 100\%$$

$$\text{molar impurity} = 2.673\,155\,205\%$$

$$\text{molar purity} = 100\% - 2.673\,155\,205\%$$

$$\text{molar purity} = 97.326\,844\,8\%$$

$$\boxed{\text{molar purity} = 97\%}$$

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**5.43.** Calculate the activity and activity coefficients for 0.330 mol fraction toluene in benzene. The vapor pressure of pure benzene is 9.657 kPa at 298 K.  $P_2^* = 3.572$  kPa for toluene. The vapor pressure for benzene above the solution is  $P_1 = 6.677$  kPa and for toluene  $P_2 = 1.214$  kPa.

**Solution:**

Given  $x_{\text{toluene}} = 0.330$ ,  $P_{\text{benzene}}^* = 9.657$  kPa,  $T = 298$  K,  $P_{\text{toluene}}^* = 3.572$  kPa

$$P_{\text{benzene}} = 6.677 \text{ kPa}, P_{\text{toluene}} = 1.214 \text{ kPa}.$$

Required:  $a_{\text{toluene}}$ ,  $a_{\text{benzene}}$ ,  $f_{\text{benzene}}$ ,  $f_{\text{toluene}}$

The activity is given by Eq. 5.75,

$$a_i = \frac{f_i}{f_i^0} = \frac{P_i}{P_i^*}$$

$$a_{\text{toluene}} = \frac{1.214 \text{ kPa}}{3.572 \text{ kPa}}$$

$$a_{\text{toluene}} = 0.3398656215$$

$$\boxed{a_{\text{toluene}} = 0.3399}$$

$$a_{\text{benzene}} = \frac{6.677 \text{ kPa}}{9.657 \text{ kPa}}$$

$$a_{\text{benzene}} = 0.6914155535$$

$$\boxed{a_{\text{benzene}} = 0.6914}$$

The activity coefficient is determined from the definition  $f_i = a_i/x_i$  where  $f_i$  is the activity coefficient (Recall that we can relate this to the expression for the Gibbs Free Energy given in Section 4.3.) .

$$f_{\text{toluene}} = \frac{a_{\text{toluene}}}{x_{\text{toluene}}}$$

$$f_{\text{toluene}} = \frac{0.339\,865\,621\,5}{0.330}$$

$$f_{\text{toluene}} = 1.029\,895\,823$$

$$\boxed{f_{\text{toluene}} = 1.03}$$

$$f_{\text{benzene}} = \frac{a_{\text{benzene}}}{x_{\text{benzene}}}$$

$$f_{\text{benzene}} = \frac{0.691\,415\,553\,5}{1 - 0.330}$$

$$f_{\text{benzene}} = 1.031\,963\,513$$

$$\boxed{f_{\text{benzene}} = 1.03}$$

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**5.44.** Calculate the mole fraction, activity, and activity coefficients for water when 11.5 g NaCl are dissolved in 100 g water at 298 K. The vapor pressure is 95.325 kPa.

**Solution:**

Given:  $m_{\text{NaCl}} = 11.5 \text{ g}$ ,  $m_{\text{H}_2\text{O}} = 100 \text{ g}$ ,  $T = 298 \text{ K}$ ,  $P = 95.325 \text{ kPa}$

Required:  $x_{\text{H}_2\text{O}}$ ,  $a_{\text{H}_2\text{O}}$ ,  $f_{\text{H}_2\text{O}}$

The mole fraction of water can be obtained from Eq. 5.79 which states that:

$$x_2 = \frac{W_2/M_2}{(W_1/M_1) + (W_2/M_2)}$$

where

$$M_{\text{H}_2\text{O}} = 2(1.00794 \text{ g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_{\text{H}_2\text{O}} = 18.01528 \text{ g mol}^{-1}$$

$$M_{\text{NaCl}} = (22.989768 \text{ g mol}^{-1}) + (35.4527 \text{ g mol}^{-1})$$

$$M_{\text{NaCl}} = 58.442468 \text{ g mol}^{-1}$$

$$x_{\text{H}_2\text{O}} = \frac{\frac{100 \cancel{\text{g}}}{18.01528 \cancel{\text{g mol}^{-1}}}}{\frac{11.5 \cancel{\text{g}}}{58.442468 \cancel{\text{g mol}^{-1}}} + \frac{100 \cancel{\text{g}}}{18.01528 \cancel{\text{g mol}^{-1}}}}$$

$$x_{\text{H}_2\text{O}} = 0.9657641291$$

$$\boxed{x_{\text{H}_2\text{O}} = 0.966}$$

As we have previously seen, the activity is given by Eq. 5.75;

$$a_i = \frac{f_i}{f_i^\circ} = \frac{P_i}{P_i^*}$$

$$a_{\text{H}_2\text{O}} = \frac{95.325 \text{ kPa}}{101.325 \text{ kPa}}$$

$$a_{\text{H}_2\text{O}} = 0.940\,784\,604$$

$$\boxed{a_{\text{H}_2\text{O}} = 0.940\,78}$$

The activity coefficient is determined from the definition  $f_i = a_i/x_i$  where  $f_i$  is the activity coefficient (Recall that we may relate this to the expression for Gibbs Free Energy from section 4.3.).

$$f_{\text{H}_2\text{O}} = \frac{a_{\text{H}_2\text{O}}}{x_{\text{H}_2\text{O}}}$$

$$f_{\text{H}_2\text{O}} = \frac{0.940\,784\,604}{0.965\,764\,129\,1}$$

$$f_{\text{H}_2\text{O}} = 0.974\,134\,962\,8$$

$$\boxed{f_{\text{H}_2\text{O}} = 0.974}$$

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**5.45.** Determine the range for the Gibbs energy of mixing for an ideal 50/50 mixture at 300 K. How does this value limit  $\Delta_{\text{mix}}H$ ?

**Solution:**

Figure 5.13 gives  $\Delta_{\text{mix}}S$  of 1 mol of an ideal solution from the pure components. For an ideal 50/50 mixture,  $x_1 = x_2 = 0.5$ , therefore by observing the figure, the maximum  $\Delta_{\text{mix}}S$  is approximately  $5.76 \text{ J K}^{-1} \text{ mol}^{-1}$ . The maximum Gibbs energy would then be then be given by Eq. 5.97 which states that:

$$-\Delta_{\text{mix}}G^{\text{id}} = T\Delta_{\text{mix}}S^{\text{id}}$$

$$-\Delta_{\text{mix}}G^{\text{id}} = (300 \text{ K})(5.76 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta_{\text{mix}}G^{\text{id}} = -1728 \text{ J mol}^{-1}$$

The range of Gibbs energy in an ideal 50/50 mixture would then be from  $\boxed{0 \text{ to } -1.73 \text{ kJ mol}^{-1}}$ .

This limits  $\Delta_{\text{mix}}H$  since the Gibbs Energy is a rather small driving force. In a non-ideal solution where  $\Delta_{\text{mix}}H=0$ , the value of  $\Delta_{\text{mix}}H$  must be negative or only slightly positive for mixing to occur.

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**5.46.** The mole fraction of a nonvolatile solute dissolved in water is 0.010. If the vapor pressure of pure water at 293 K is 2.339 kPa and that of the solution is 2.269 kPa, calculate the activity and activity coefficient of water.

**Solution:**

Given:  $x_{\text{solute}} = 0.010$ ,  $T = 293 \text{ K}$ ,  $P_{\text{H}_2\text{O}}^* = 2.339 \text{ kPa}$ ,  $P_{\text{H}_2\text{O}} = 2.269 \text{ kPa}$

Required:  $a_{\text{H}_2\text{O}}$ ,  $f_{\text{H}_2\text{O}}$

Recall that the activity is given by Eq. 5.75:

$$a_i = \frac{f_i}{f_i^o} = \frac{P_i}{P_i^*}$$

$$a_{\text{H}_2\text{O}} = \frac{2.269 \text{ kPa}}{2.339 \text{ kPa}}$$

$$a_{\text{H}_2\text{O}} = 0.970\,072\,680\,6$$

$$\boxed{a_{\text{H}_2\text{O}} = 0.9701}$$

The activity coefficient is determined from the definition  $f_i = a_i/x_i$  where  $f_i$  is the activity coefficient (In chapter 4, we were given an expression for the Gibbs Free Energy which can be related back to the activity). Therefore,

$$f_{\text{H}_2\text{O}} = \frac{a_{\text{H}_2\text{O}}}{x_{\text{H}_2\text{O}}}$$

$$f_{\text{H}_2\text{O}} = \frac{0.970\,072\,680\,6}{1 - 0.010}$$

$$f_{\text{H}_2\text{O}} = 0.979\,871\,394\,6$$

$$\boxed{f_{\text{H}_2\text{O}} = 0.980}$$

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**5.47.** A nonideal solution contains  $n_A$  of substance A and  $n_B$  of substance B and the mole fractions of A and B are  $x_A$  and  $x_B$ . The Gibbs energy of the solution is given by the equation

$$G = n_A \mu_A^o + n_B \mu_B^o + RT(n_A \ln x_A + n_B \ln x_B) + C n_A n_B / (n_A + n_B)$$

where  $C$  is a constant and describes the pair interaction.

**a.** Derive an equation for  $\mu_A$  in the solution in terms of the quantities on the right-hand side. {Hint:  $(\partial \ln x_A / \partial n_A)_{n_B} = (1/n_A) - [1/(n_A + n_B)]$ . }

**b.** Derive a similar expression for the activity coefficient of A. Specify the conditions when the activity coefficient equals unity.

**Solution:**

Find the value of  $\mu_A$  such that  $\mu_A + \mu_B = G$  is equal to the expression given in the problem. First we can start by outlining the partial derivative for  $\mu_A$ ;

$$\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{n_B, T, P}$$

$$\mu_A = \mu_A^* + RT \left( \ln x_A + n_A \left( \frac{\partial \ln x_A}{\partial n_A} \right)_{n_B} + n_B \left( \frac{\partial \ln x_B}{\partial n_A} \right)_{n_B} \right) + C \left( \frac{n_B (n_A + n_B) - n_A n_B}{(n_A + n_B)^2} \right)$$

Using the hint given in the problem, we recognize that the derivative of  $\ln x_A$  is:

$$\left( \frac{\partial \ln x_A}{\partial n_A} \right)_{n_B} = \left( \frac{\partial \ln \left( \frac{n_A}{n_A + n_B} \right)}{\partial n_A} \right)_{n_B} = \left( \frac{\partial}{\partial n_A} (\ln n_A - \ln (n_A + n_B)) \right)_{n_B}$$

$$\left( \frac{\partial \ln x_A}{\partial n_A} \right)_{n_B} = \frac{1}{n_A} - \frac{1}{n_A + n_B}$$

Therefore, the expression for  $\ln x_B$  is:

$$\left( \frac{\partial \ln x_B}{\partial n_A} \right)_{n_B} = \left( \frac{\partial \ln \left( \frac{n_B}{n_A + n_B} \right)}{\partial n_A} \right)_{n_B} = \left( \frac{\partial}{\partial n_A} (\ln n_B - \ln (n_A + n_B)) \right)_{n_B}$$

$$\left( \frac{\partial \ln x_B}{\partial n_A} \right)_{n_B} = -\frac{1}{n_A + n_B}$$

Substituting the above into the initial equation and simplifying, we can obtain an equation for  $\mu_A$ .

$$\mu_A = \mu_A^* + RT \left( \ln x_A + n_A \left( \frac{1}{n_A} - \frac{1}{n_A + n_B} \right) + n_B \left( -\frac{1}{n_A + n_B} \right) \right) + C \left( \frac{n_B (n_A + n_B) - n_A n_B}{(n_A + n_B)^2} \right)$$

$$\mu_A = \mu_A^* + RT \left( \ln x_A + \cancel{\frac{n_A}{n_A}} - \frac{n_A}{n_A + n_B} - \frac{n_B}{n_A + n_B} \right) + C \left( \frac{\cancel{n_A n_B} + n_B^2 - \cancel{n_A n_B}}{(n_A + n_B)^2} \right)$$

$$\mu_A = \mu_A^* + RT \left( \ln x_A + 1 - \frac{n_A + n_B}{n_A + n_B} \right) + \frac{C n_B^2}{(n_A + n_B)^2}$$

$$\mu_A = \mu_A^* + RT \left( \ln x_A + 1 - \left( \frac{\cancel{n_A + n_B}}{\cancel{n_A + n_B}} \right) \right) + \frac{C n_B^2}{(n_A + n_B)^2}$$

$$\boxed{\mu_A = \mu_A^* + RT \ln x_A + C x_B^2}$$

To obtain an expression for the activity coefficient of A we can compare the expression in part a with Eq. 5.102 which states that:

$$\mu_i - \mu_{i,\text{id}} = RT \ln \frac{a_i}{x_i}$$

From Eq. 5.103 we can see that,

$$f_i = \frac{a_i}{x_i} \quad \text{and} \quad f_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1$$

$$\mu_i - \mu_{i,\text{id}} = RT \ln f_i$$

$$\mu_i = \mu_{i,\text{id}} + RT \ln f_i$$

$$\mu_A = \mu_A^* + RT \ln f_A$$

By comparison,

$$RT \ln f_A = Cx_B^2$$

$$f_A = e^{\frac{Cx_B^2}{RT}}$$

$$f_A = 1, \text{ as } x_B \rightarrow 0$$

This corresponds to pure A. In a very dilute solution of A in B, we also expect  $f_A \rightarrow 1$ . In that case,

$$\mu_A^{*'} = \lim_{x_A \rightarrow 0} (\mu_A - RT \ln x_A)$$

Substitution of the expression above into the previous yields;

$$\mu_A^{*'} = \lim_{x_B \rightarrow 1} (\mu_A^* + Cx_B^2) = \mu_A^* + C$$

Therefore,

$$\mu = \mu_A^{*'} + RT \ln x_A + C(x_B^2 - 1) = \mu_A^* + RT \ln x_A + RT \ln f_A$$

$$\ln f_A = \frac{C(x_B^2 - 1)}{RT} = 0, \text{ when } x_B \rightarrow 1$$

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**5.48.** Calculate the mole fraction solubility of naphthalene at 25 °C in a liquid with which it forms an ideal solution. The  $\Delta_{\text{fus}}H = 19.0 \text{ kJ mol}^{-1}$  for naphthalene at 25 °C. Its normal melting point is 80.2 °C.

**Solution:**

Given:  $T = 298.15 \text{ K}$ ,  $\Delta_{\text{fus}}H = 19.0 \text{ kJ mol}^{-1}$ ,  $T_m = 80.2 \text{ °C} = 353.35 \text{ K}$

Required:  $x_n$

To solve this problem, we must use the expression for the mole fraction of a solvent in relation to the freezing point of an ideal solution and to the freezing point of the pure solvent. This is given by Eq. 5.115:

$$\ln x_1 = -\frac{\Delta_{\text{fus}}H_m}{R} \left( \frac{1}{T_f^*} - \frac{1}{T} \right)$$

Solving for  $x_n$ , we obtain,

$$x_n = e^{\frac{\Delta_{\text{fus}}H_m}{R} \left( \frac{1}{T_f^*} - \frac{1}{T} \right)}$$

$$x_n = e^{\frac{19.0 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{353.35 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)}$$

$$x_n = e^{-1.19733763}$$

$$x_n = 0.3019971708$$

$$\boxed{x_n = 0.302}$$

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- 5.49.** Using Henry's law, determine the difference between the freezing point of pure water and water saturated with air at 1 atm. For  $N_2$  at 298.15 K,

$$(k'')^{-1} = 2.17 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1}$$

For  $O_2$  at 298.15 K,

$$(k'')^{-1} = 1.02 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1}$$

**Solution:**

Given:  $T = 298.15 \text{ K}$ ,  $P = 1 \text{ atm}$ ,

$$(k'')^{-1}_{N_2} = 2.17 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1}, (k'')^{-1}_{O_2} = 1.02 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1}$$

Required:  $\Delta_{\text{fus}} T$

We have previously seen that Henry's Law is given by Eq. 5.27 stating that:

$$P_2 = k'' c_2$$

We can use Henry's Law to determine the concentrations of  $N_2$  and  $O_2$  in water. Rearranging, we obtain,

$$c_2 = P_2 (k'')^{-1}$$

The partial pressures for  $N_2$  and  $O_2$  are found under the assumption that  $N_2$  gives rise to a 80% rise of the pressure and that  $O_2$  gives rise to a 20% rise of the pressure. These are the fractions most commonly used for the composition of air.

$$c_{N_2} = 0.80 (101\,325 \text{ Pa}) (2.17 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1})$$

$$c_{N_2} = 1.759\,002 \times 10^{-3} \text{ mol dm}^{-3}$$

$$c_{O_2} = 0.20 (101\,325 \text{ Pa}) (1.02 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pa}^{-1})$$

$$c_{O_2} = 2.067\,03 \times 10^{-4} \text{ mol dm}^{-3}$$

The total concentration of air in water will approach  $m_2$ , the value for molality.

$$c = c_{\text{N}_2} + c_{\text{O}_2}$$

$$c = 1.759\,002 \times 10^{-3} \text{ mol dm}^{-3} + 2.067\,03 \times 10^{-4} \text{ mol dm}^{-3}$$

$$c = 1.965\,705 \times 10^{-3} \text{ mol dm}^{-3}$$

$$c \approx m_2$$

The freezing point depression is given by Eq. 5.121, where  $K_f$  is the freezing point depression constant for water provided by Table 5.2.

$$\Delta_{\text{fus}}T = K_f m_2$$

$$\Delta_{\text{fus}}T = (1.86 \text{ K } \cancel{\text{kg}} \cancel{\text{mol}^{-1}}) (1.965\,705 \times 10^{-3} \cancel{\text{mol}} \cancel{\text{kg}^{-1}})$$

$$\Delta_{\text{fus}}T = 3.656\,211\,3 \times 10^{-3} \text{ K}$$

$$\boxed{\Delta_{\text{fus}}T = -3.66 \times 10^{-3} \text{ K}}$$

The freezing point is decreased by  $3.66 \times 10^{-3} \text{ K}$ .

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**5.50.** Using van't Hoff's equation, calculate the osmotic pressure developed if 6.00 g of urea,  $(\text{NH}_2)_2\text{CO}$ , is dissolved in 1.00 dm<sup>3</sup> of solution at 27 °C.

**Solution:**

Given:  $m = 6.00 \text{ g}$ ,  $V = 1.00 \text{ dm}^3$ ,  $T = 300.15 \text{ K}$

Required:  $\pi$

The van't Hoff's Equation for osmotic pressure is given by Eq. 5.134:

$$\pi = \frac{n_2 RT}{V} \quad \text{or} \quad \pi = cRT$$

$$\text{where, } n = \frac{m}{M}$$

$$\pi = \frac{mRT}{MV}$$

$$M = 2(14.00674 \text{ g mol}^{-1}) + 4(1.00794 \text{ g mol}^{-1}) + (12.011 \text{ g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M = 60.05564 \text{ g mol}^{-1}$$

$$\pi = \frac{(6.00 \text{ g})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300.15 \text{ K})}{(60.05564 \text{ g mol}^{-1})\left(1.00 \text{ dm}^3 \times 10^{-3} \frac{\text{m}^3}{\text{dm}^3}\right)}$$

$$\pi = 249203.9049 \text{ J m}^{-3}$$

$$\text{where } 1 \text{ J} = \text{kg m}^2 \text{ s}^{-2} \text{ and } 1 \text{ Pa} = \text{kg m}^{-1} \text{ s}^{-2}$$

$$1 \text{ J m}^{-3} = 1 \text{ kg m}^2 \text{ s}^{-2} \text{ m}^{-3} = 1 \text{ kg m}^{-1} \text{ s}^{-2} = 1 \text{ Pa}$$

$$\pi = 249203.9049 \text{ Pa}$$

$$\boxed{\pi = 249 \text{ kPa}}$$

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**5.51.** The apparent value of  $K_f$  in 1.50-molal aqueous sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) solution is  $2.17 \text{ K kg mol}^{-1}$ . The solution does not behave ideally; calculate its activity and activity coefficient ( $\Delta_{\text{fus}}H^\circ = 6009.5 \text{ J mol}^{-1}$ ).

**Solution:**

Given:  $K_f = 2.17 \text{ K kg mol}^{-1}$ ,  $m = 1.50 \text{ mol kg}^{-1}$ ,  $\Delta_{\text{fus}}H^\circ = 6009.5 \text{ J mol}^{-1}$

Required:  $a$ ,  $f$

To solve for the activity and activity coefficient we start by obtaining  $\Delta_{\text{fus}}T$ . We know that the freezing point depression is given by Eq. 5.121:

$$\Delta_{\text{fus}}T = K_f m_2$$

$$\Delta_{\text{fus}}T = (2.17 \text{ K } \cancel{\text{kg}} \cancel{\text{mol}^{-1}})(1.50 \cancel{\text{mol}} \cancel{\text{kg}^{-1}})$$

$$\Delta_{\text{fus}}T = 3.255 \text{ K}$$

The freezing point depression is  $T_f^* - T = \Delta_{\text{fus}}T$ . Since  $\Delta_{\text{fus}}T$  is small in comparison to  $T_f^*$ , we may set the product  $TT_f^* \approx T_f^{*2}$ . Substituting the value of  $\Delta_{\text{fus}}T$  into Eq. 5.115, and replacing  $a_1$  for  $x_1$ , we can solve for the activity.



$$\ln x_1 = \frac{\Delta_{\text{fus}} H_m}{R} \left( \frac{1}{T_f^*} - \frac{1}{T} \right)$$

$$\ln a_1 = \frac{\Delta_{\text{fus}} H_m}{R} \left( \frac{T - T_f^*}{T_f^* T} \right)$$

$$\ln a_1 = \frac{\Delta_{\text{fus}} H_m}{R} \left( -\frac{\Delta_{\text{fus}} T}{T_f^{*2}} \right)$$

$$a_1 = e^{-\frac{\Delta_{\text{fus}} H_m}{R} \frac{\Delta_{\text{fus}} T}{T_f^{*2}}}$$

$$a_1 = e^{-\frac{6009.5 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \frac{3.255 \text{ K}}{(273.15 \text{ K})^2}}$$

$$a_1 = e^{-0.0315319468}$$

$$a_1 = 0.9689600008$$

$$\boxed{a_1 = 0.969}$$

The activity coefficient is determined from the definition  $f_i = a_i/x_i$  where  $f_i$  is the activity coefficient. (See Section 4.3)

$$x_1 = \frac{m_1}{m_1 + m_2}$$

$$M_{\text{sucrose}} = 12(12.011 \text{ g mol}^{-1}) + 22(1.007 \text{ 94 g mol}^{-1}) + 11(15.9994 \text{ g mol}^{-1})$$

$$M_{\text{sucrose}} = 343.300 \text{ 08 g mol}^{-1}$$

$$M_{\text{H}_2\text{O}} = 2(1.007 \text{ 94 g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_{\text{H}_2\text{O}} = 18.015 \text{ 28 g mol}^{-1}$$

$$x_1 = \frac{\frac{18.015 \text{ 28 } \cancel{\text{g}} \text{ mol}^{-1}}{343.300 \text{ 08 } \cancel{\text{g}} \text{ mol}^{-1}}}{\frac{18.015 \text{ 28 } \cancel{\text{g}} \text{ mol}^{-1}}{343.300 \text{ 08 } \cancel{\text{g}} \text{ mol}^{-1}} + (1.50 \times 10^3 \cancel{\text{mol}} \cancel{\text{g}}^{-1})^{-1}}$$

$$x_1 = 0.987 \text{ 455 334 4}$$

$$f = \frac{a_1}{x_1}$$

$$f = \frac{0.968 \text{ 960 000 8}}{0.987 \text{ 455 334 4}}$$

$$f = 0.981 \text{ 269 701 1}$$

$$\boxed{f = 0.981}$$

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**5.52.** A 0.85-g sample is dissolved in 0.150 kg of bromobenzene. Determine the molar mass of the solute if the solution boils at 429.0 K at 1 atm pressure. The normal boiling point of bromobenzene is 428.1 K and the boiling point elevation constant is 6.26 K kg mol<sup>-1</sup>.

**Solution:**

Given:  $m = 0.85$  g,  $m_{\text{bromobenzene}} = 0.150$  kg,  $T_{b,\text{solution}} = 429.0$  K,  $P = 1$  atm,

$$T_{b,\text{bromobenzene}} = 428.1 \text{ K}, K_b = 6.26 \text{ K kg mol}^{-1}$$

Required:  $M_{\text{solute}}$

To solve for the molar mass of the solute, we start by obtaining the molality,  $m_2$ , from the expression for the boiling point elevation, given by Eq. 5.126:

$$\Delta_{\text{vap}} T = K_b m_2$$

$$m_2 = \frac{\Delta_{\text{vap}} T}{K_b}$$

$$m_2 = \frac{429.0 \cancel{\text{ K}} - 428.1 \cancel{\text{ K}}}{6.26 \cancel{\text{ K}} \text{ kg mol}^{-1}}$$

$$m_2 = 0.1437699681 \text{ mol kg}^{-1}$$

The mass of the solute per kilogram of solvent can be found using the following expression.

$$\frac{m_{\text{solute}}}{m_{\text{bromobenzene}}} = \frac{0.85 \times 10^{-3} \cancel{\text{ kg}}}{0.150 \cancel{\text{ kg}}}$$

$$\frac{m_{\text{solute}}}{m_{\text{bromobenzene}}} = 5.666667 \times 10^{-3}$$

Solving for the molar mass by using the ratio of solute to solvent, we obtain,

$$M = \frac{5.666\,667 \times 10^{-3}}{0.143\,769\,968\,1 \text{ mol kg}^{-1}}$$

$$M = 0.039\,414\,814\,8 \cancel{\text{ kg}} \text{ mol}^{-1} \times 10^3 \frac{\text{g}}{\cancel{\text{ kg}}}$$

$$M = 39.414\,814\,8 \text{ g mol}^{-1}$$

$$\boxed{M = 39 \text{ g mol}^{-1}}$$

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**5.53.** If in a colligative properties experiment a solute dissociates, a term  $i$  known as van't Hoff's factor, which is the total concentration of ions divided by the nominal concentration, must be included as a factor. Thus, for the lowering of the freezing point,  $\Delta_{fus}T = imK_f$ . Derive an expression that relates to the degree of dissociation  $\alpha$  and to  $\nu$ , the number of particles that would be produced if the solute were completely dissociated. Then calculate van't Hoff's  $i$  factor and  $\alpha$  for a 0.010-m solution of HCl that freezes at 273.114 K.

**Solution:**

Given:  $\Delta_{fus}T = imK_f$ ,  $m_{\text{HCl}} = 0.010m$ ,  $T_f = 273.114 \text{ K}$

Required: expression that relates to the degree of dissociation  $\alpha$  and to  $\nu$ , calculate  $i$ ,  $\alpha$  for HCl

For this particular problem, we consider the dissociation of any general compound  $A_xB_y$  to be given by:

	$A_xB_y$	$\rightleftharpoons$	$xA^{z+}$	+	$yB^{z-}$	
$m_{\text{initial}}$	$m$		0		0	$\text{mol kg}^{-1}$
$m_{\text{dissociation}}$	$m - \alpha m$		$x\alpha m$		$y\alpha m$	$\text{mol kg}^{-1}$

The total molality can therefore be expressed as,

$$m_{\text{total}} = m - \alpha m + x\alpha m + y\alpha m$$

$$m_{\text{total}} = m(1 - \alpha + x\alpha + y\alpha) \text{ mol kg}^{-1}$$

The term  $i$  known as van't Hoff's factor, is the total concentration of ions divided by the nominal concentration. Solving for  $i$ , we obtain,

$$i = \frac{m_{\text{total}}}{m_{\text{initial}}}$$

$$i = \frac{\cancel{m} (1 - \alpha + x\alpha + y\alpha) \cancel{\text{mol kg}^{-1}}}{\cancel{m} \cancel{\text{mol kg}^{-1}}}$$

$$i = 1 - \alpha + x\alpha + y\alpha$$

$\nu$  is the total number of moles of reactants present,  $\nu = x + y$ , therefore we can obtain an expression of  $\alpha$  in terms of  $\nu$ .

$$i = 1 - \alpha + \alpha v$$

$$i = 1 + \alpha(v - 1)$$

$$\boxed{\alpha = \frac{i - 1}{v - 1}}$$

In the case of HCl, we use  $K_f$  for water, provided by table 5.2.

$$i = \frac{\Delta_{fus} T}{m K_f}$$

$$i = \frac{273.15 \text{ K} - 273.114 \text{ K}}{(0.010 \text{ mol kg}^{-1}) 1.86 \text{ K kg mol}^{-1}}$$

$$i = 1.935\,483\,871$$

$$\boxed{i = 1.94}$$

The dissociation of HCl is complete and gives  $v = 2$ ,

$$\alpha = \frac{1.935\,483\,871 - 1}{2 - 1}$$

$$\alpha = 0.935\,483\,871$$

$$\boxed{\alpha = 0.935}$$

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**5.54.** In an osmotic pressure experiment to determine the molar mass of a sugar, the following data were taken at 20 °C:

$\pi/\text{atm}$	2.59	5.06	7.61	12.75	18.13	23.72
$m_2 V^{-1}/\text{g dm}^{-3}$	33.5	65.7	96.5	155	209	259

Estimate the molar mass of the sugar. If the sugar is sucrose, what is the percentage error and why?

**Solution:**

Given:  $T = 293.15 \text{ K}$

Required:  $M$ , *percent error*

The van't Hoff's equation for osmotic pressure is given by Eq. 5.134 which states that:

$$\pi = \frac{n_2 RT}{V} \quad \text{or} \quad \pi = cRT$$

$$\text{where, } n = \frac{m}{M}$$

$$\pi = \frac{m_2 RT}{M_2 V}$$

We can rearrange the above expression to isolate for  $M_2$ ,

$$M_2 = \frac{m_2 RT}{\pi V}$$

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**5.55.** When 3.78 g of a nonvolatile solute is dissolved in 300.0 g of water, the freezing point depression is 0.646 °C. Calculate the molar mass of the compound.  $K_f = 1.856 \text{ K kg mol}^{-1}$ .

**Solution:**

Given:  $m = 3.78 \text{ g}$ ,  $m_{\text{H}_2\text{O}} = 300.0 \text{ g}$ ,  $\Delta_{\text{fus}}T = 0.646 \text{ °C} = 0.646 \text{ K}$ ,  $K_f = 1.856 \text{ K kg mol}^{-1}$

Required:  $M$

To solve this problem, we must simply use Eq. 5.122:

$$M_2 = \frac{K_f W_2}{\Delta_{\text{fus}} T W_1}$$

$$M_2 = \frac{(1.856 \text{ K kg mol}^{-1})(3.78 \text{ g})}{(0.646 \text{ K})(300.0 \text{ g})}$$

$$M_2 = 0.036\,200\,619\,2 \text{ } \cancel{\text{kg}} \text{ mol}^{-1} \times 10^3 \frac{\text{g}}{\cancel{\text{kg}}}$$

$$M_2 = 36.200\,619\,2 \text{ g mol}^{-1}$$

$$\boxed{M_2 = 36.2 \text{ g mol}^{-1}}$$

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**5.56.** Calculate the elevation in the boiling point of water if 6.09 g of a nonvolatile compound with molar mass of  $187.4 \text{ g mol}^{-1}$  is dissolved in 250.0 g of water. Compare the values obtained using Eq. 5.125 and Eq. 5.126. The value of  $K_b = 0.541 \text{ K kg mol}^{-1}$ ;  $\Delta_{\text{vap}}H = 40.66 \text{ kJ mol}^{-1}$ .

**Solution:**

Given:  $m = 6.09 \text{ g}$ ,  $m_{\text{H}_2\text{O}} = 250.0 \text{ g}$ ,  $M = 187.4 \text{ g mol}^{-1}$ ,

$$K_b = 0.541 \text{ K kg mol}^{-1}, \Delta_{\text{vap}}H = 40.66 \text{ kJ mol}^{-1}$$

Required:  $\Delta_{\text{vap}}T$

To obtain  $\Delta_{\text{vap}}T$  from Eq. 5.125, we first need to find the value for  $x_1$ ,

$$\ln x_1 = \frac{\Delta_{\text{vap}}H_m}{R} \left( \frac{1}{T} - \frac{1}{T_b^*} \right)$$

The mole fraction of water can be determined by using,

$$x_1 = \frac{m_1/M_1}{(m_1/M_1) + (m_2/M_2)}$$

where

$$M_{\text{H}_2\text{O}} = 2(1.00794 \text{ g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_{\text{H}_2\text{O}} = 18.01528 \text{ g mol}^{-1}$$

$$x_{\text{H}_2\text{O}} = \frac{\frac{250.0 \cancel{\text{g}}}{18.01528 \cancel{\text{g mol}^{-1}}}}{\frac{250.0 \cancel{\text{g}}}{18.01528 \cancel{\text{g mol}^{-1}}} + \frac{6.09 \cancel{\text{g}}}{187.4 \cancel{\text{g mol}^{-1}}}}$$

$$x_{\text{H}_2\text{O}} = 0.9976640264$$

Solving for  $\Delta_{\text{vap}}T$ , we obtain,

$$\frac{1}{T} = \frac{R}{\Delta_{\text{vap}} H_m} \ln x_1 + \frac{1}{T_b^*}$$

$$\frac{1}{T} = \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{40.66 \times 10^3 \text{ J mol}^{-1}} \ln(0.997\,664\,026\,4) + \frac{1}{373.15 \text{ K}}$$

$$\frac{1}{T} = 0.002\,679\,409\,2 \text{ K}^{-1}$$

$$T = 373.216\,602\,2 \text{ K}$$

$$\Delta_{\text{vap}} T = 373.216\,602\,2 \text{ K} - 373.15 \text{ K}$$

$$\Delta_{\text{vap}} T = 0.066\,602\,2 \text{ K}$$

$$\boxed{\Delta_{\text{vap}} T = 6.66 \times 10^{-2} \text{ K}}$$

We can also obtain  $\Delta_{\text{vap}} T$  from Eq. 5.126. However, we first need to find the value for  $m_2$ ,

$$\Delta_{\text{vap}} T = K_b m_2$$

The molality can be obtained using,

$$m_2 = \frac{n_2}{m}$$

$$m_2 = \frac{\frac{6.09 \text{ g}}{187.4 \text{ g mol}^{-1}}}{250.0 \times 10^{-3} \text{ kg}}$$

$$m_2 = 0.129\,989\,327\,6 \text{ mol kg}^{-1}$$

Solving for  $\Delta_{\text{vap}} T$ , we obtain,

$$\Delta_{\text{vap}} T = (0.541 \text{ K } \cancel{\text{kg}} \cancel{\text{mol}}^{-1}) (0.129\,989\,327\,6 \cancel{\text{mol}} \cancel{\text{kg}}^{-1})$$

$$\Delta_{\text{vap}} T = 0.070\,324\,226\,3 \text{ K}$$

$$\boxed{\Delta_{\text{vap}} T = 7.03 \text{ K}}$$

[Back to Problem 5.56](#)

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- 5.57.** Suppose that you find in the older literature the vapor pressure  $P$  of a liquid with molar mass of  $63.9 \times 10^{-3} \text{ kg mol}^{-1}$  listed with  $P$  in mmHg as

$$\log P = 5.4672 - 1427.3 T^{-1} - 3169.3 T^{-2}$$

The densities of the liquid and vapor phases are  $0.819 \text{ kg dm}^{-3}$  and  $3.15 \times 10^{-4} \text{ kg dm}^{-3}$ , respectively. Calculate the  $\Delta_{\text{vap}}H$  at the normal boiling point, 398.4 K. How do you handle the fact that  $P$  is listed in mmHg?

**Solution:**

Given:  $M = 63.9 \times 10^{-3} \text{ kg mol}^{-1}$ ,  $\rho_{\text{liquid}} = 0.819 \text{ kg dm}^{-3}$ ,  $\rho_{\text{vapor}} = 3.15 \times 10^{-4} \text{ kg dm}^{-3}$ ,  $T_b = 398.4 \text{ K}$

Required:  $\Delta_{\text{vap}}H$

We can use the Clapeyron equation to solve this problem, given by Eq. 5.9:

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

Since the boiling point is given at 1 atm, it is appropriate for us to express pressure in terms of atmospheres. Since  $1 \text{ mmHg} = 1 \text{ Torr}$ , then;

$$\log(P / \text{Torr}) = \log\left(P / \text{atm} \times \frac{1 \text{ atm}}{760 \text{ Torr}}\right)$$

$$\log(P / \text{Torr}) = \log(P / \text{atm}) + \log\left(\frac{1 \text{ atm}}{760 \text{ Torr}}\right)$$

The derivative of this expression shows that it does not matter how pressure is expressed as long as we are only considering the ultimate CHANGE in pressure.

$$\frac{d \log P}{dT} = \log_{10} e \frac{1}{P} \frac{dP}{dT}$$

$$\frac{dP}{dT} = \frac{P}{\log_{10} e} \frac{d \log P}{dT}$$

$$\frac{dP}{dT} = \frac{P}{\log_{10} e} \frac{d}{dT} (5.4672 - 1427.3 T^{-1} - 3169.3 T^{-2})$$

$$\frac{dP}{dT} = \frac{P}{\log_{10} e} (1427.3 T^{-2} + 2(3169.3) T^{-3})$$

$$\frac{dP}{dT} = \frac{P}{(0.434\ 294\ 481\ 9)} (1427.3\ \text{K}\ T^{-2} + 6338.6\ \text{K}^2\ T^{-3})$$

We can now use the Clapeyron equation at  $T_b$  where  $P = 1\ \text{atm}$  to solve.

$$\frac{dP}{dT} = \frac{1\ \text{atm}}{(0.434\ 294\ 481\ 9)} (1427.3\ \text{K} (398.4\ \text{K})^{-2} + 6338.6\ \text{K}^2 (398.4\ \text{K})^{-3})$$

$$\frac{dP}{dT} = 0.020\ 936\ 621\ 5\ \text{atm}\ \text{K}^{-1}$$

We can solve for  $\Delta V_m$  using the densities given in the problem above to get;

$$\rho = \frac{M}{V_m}$$

$$V_{m \text{ liquid}} = \frac{M}{\rho_{\text{liquid}}}$$

$$V_{m \text{ liquid}} = \frac{63.9 \times 10^{-3} \cancel{\text{kg}} \text{ mol}^{-1}}{0.819 \cancel{\text{kg}} \text{ dm}^{-3}}$$

$$V_{m \text{ liquid}} = 0.078\,021\,978 \text{ dm}^3 \text{ mol}^{-1}$$

$$V_{m \text{ vapor}} = \frac{M}{\rho_{m \text{ vapor}}}$$

$$V_{m \text{ vapor}} = \frac{63.9 \times 10^{-3} \cancel{\text{kg}} \text{ mol}^{-1}}{3.15 \times 10^{-4} \cancel{\text{kg}} \text{ dm}^{-3}}$$

$$V_{m \text{ vapor}} = 202.857\,142\,9 \text{ dm}^3 \text{ mol}^{-1}$$

$$\Delta V_m = V_{m \text{ vapor}} - V_{m \text{ liquid}}$$

$$\Delta V_m = 202.857\,142\,9 \text{ dm}^3 \text{ mol}^{-1} - 0.078\,021\,978 \text{ dm}^3 \text{ mol}^{-1}$$

$$\Delta V_m = 202.779\,120\,9 \text{ dm}^3 \text{ mol}^{-1}$$

Rearranging Eq. 5.9, we can solve for  $\Delta_{\text{vap}}H$  which yields,

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

$$\Delta H_m = T \Delta V_m \frac{dP}{dT}$$

$$\Delta H_m = (398.4 \text{ K}) (202.779 120 9 \text{ dm}^3 \text{ mol}^{-1}) (0.020 936 621 5 \text{ atm K}^{-1})$$

$$\Delta H_m = 1691.411 065 \text{ atm dm}^3 \text{ mol}^{-1}$$

$$1 \text{ atm dm}^3 = 101.325 \text{ J}$$

$$\Delta H_m = 1691.411 065 \times \frac{101.325 \text{ J}}{\cancel{\text{atm}} \cancel{\text{dm}^3}} \text{ atm } \cancel{\text{dm}^3} \text{ mol}^{-1}$$

$$\Delta H_m = 171 382.2262 \text{ J mol}^{-1}$$

$$\boxed{\Delta H_m = 171.4 \text{ kJ mol}^{-1}}$$

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**5.58.** Calculate the osmotic pressure of seawater using the data of Table 5.5. Assume a temperature of 298 K and that the concentration of the additional salts not listed does not substantially contribute to the osmotic pressure.

**Solution:**

Given: Table 5.5,  $T=298\text{ K}$

Required:  $\pi$

The van't Hoff's Equation for osmotic pressure is given by Eq. 5.134 which states that:

$$\pi = \frac{n_2 RT}{V} \quad \text{or} \quad \pi = cRT$$

To solve for the osmotic pressure of seawater, we must first begin by determining the *total* molar concentration using data given in Table 5.5.

$$c = c_{\text{Cl}} + c_{\text{Na}} + c_{\text{Mg}} + c_{\text{S}} + c_{\text{Ca}} + c_{\text{K}} + c_{\text{Br}} + c_{\text{C}}$$

$$c = (0.536 + 0.457 + 0.0555 + 0.0276 + 0.010 + 0.0097 + 0.00081 + 0.0023) \text{ mol dm}^{-3}$$

$$c = 1.09891 \text{ mol dm}^{-3}$$

$$\pi = (1.09891 \text{ mol dm}^{-3}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$$

$$\pi = 2722.792384 \text{ J dm}^{-3} \times 10^3 \frac{\text{m}^{-3}}{\text{dm}^{-3}}$$

$$\text{where } 1 \text{ J} = \text{kg m}^2 \text{ s}^{-2} \text{ and } 1 \text{ Pa} = \text{kg m}^{-1} \text{ s}^{-2}$$

$$1 \text{ J m}^{-3} = 1 \text{ kg m}^2 \text{ s}^{-2} \text{ m}^{-3} = 1 \text{ kg m}^{-1} \text{ s}^{-2} = 1 \text{ Pa}$$

$$\pi = 2722.792384 \text{ Pa}$$

$$\pi = 2722.792384 \text{ kPa}$$

$$\boxed{\pi = 2.72 \times 10^3 \text{ kPa}}$$

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CHAPTER 6

Phase Equilibria

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Physical Chemistry

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Problems and Solutions

**Chapter 6**

*\*problems with an asterisk are slightly more demanding*

**Number of Components and Degrees of Freedom**

**6.1.** In Figure 6.1, in the region marked *orthorhombic*, how many degrees of freedom exist? How many components are present? How many phases? How many phases exist in the region marked *monoclinic*?

[Solution](#)

**6.2.** What is the composition of the two-phase region in Figure 6.14? How many degrees of freedom exist in this region?

[Solution](#)

**6.3.** Determine the number of degrees of freedom for the following systems:

- a. A solution of potassium chloride in water at the equilibrium pressure.
- b. A solution of potassium chloride and sodium chloride at 298 K at 1 atm pressure.
- c. Ice in a solution of water and alcohol.

[Solution](#)

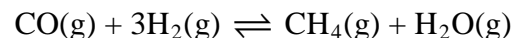
**6.4.** How many components are present in a water solution of sodium acetate?

[Solution](#)

**6.5.** How many components are present in the system  $\text{CaCO}_3\text{--CaO--CO}_2$ ?

[Solution](#)

**6.6.** How many components are present in the following system?



[Solution](#)

- 6.7.** A certain substance exists in two solid phases A and B and also in the liquid and gaseous states. Construct a  $P$ - $T$  phase diagram indicating the regions of stable existence for each phase from the following triple-point data:

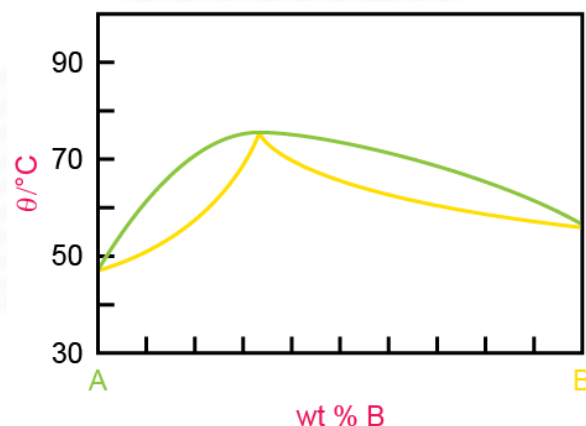
T/K	P/kPa	Phase in Equilibrium
200	100	A, B, gas
300	300	A, B, liquid
400	400	B, liquid, gas

[Solution](#)

### Use of the Lever Rule; Distillation

- 6.8.** Answer the following questions, using the accompanying figure.

- A liquid mixture consists of 33 g of component A and 99 g of component B. At what temperature would the mixture begin to boil?
- Under the conditions in (a), what is the composition of the vapor when boiling first occurs?
- If the distillation is continued until the boiling point is raised by 5.0 °C, what would be the composition of the liquid left in the still?



- Under the conditions in (c), what are the composition and mass of the two components collected over the initial 5.0 °C interval?

[Solution](#)

- 6.9.** From the data of Figure 6.14, calculate the ratio of the mass of the water-rich layer to that of the nicotine-rich layer, for a 40 wt % water–nicotine mixture at 350 K.

[Solution](#)

- 6.10.** The ratio of the mass of chlorobenzene to that of water collected in a steam distillation is 1.93 when the mixture was boiled at 343.85 K and 56.434 kPa. If the vapor pressure of water at this temperature is 43.102 kPa, calculate the molar mass of chlorobenzene.

[Solution](#)

- 6.11. a.** Do the actual derivation of Eq. 6.11 from Eq. 6.8.

**b.** From Eq. 6.8 derive an expression that gives you the ratio of the mass of two volatile components, 1 and 2, in terms of their mole fractions in the vapor and their molar masses.

[Solution](#)

- 6.12.** Obtain an expression for the ratio of masses of the materials distilled in a steam distillation in terms of the molar masses and the partial pressures of the two components.

[Solution](#)

- 6.13.** Under atmospheric pressure 1 kg of pure naphthalene is to be prepared by steam distillation at 372.4 K. What mass of steam is required to perform this purification? The vapor pressure of pure water at 372.4 K is 98.805 kPa.

[Solution](#)

- 6.14.** The vapor pressure of water at 343.85 K is 43.102 kPa. A certain mixture of chlorobenzene and water boils at 343.85 K under a reduced pressure of 56.434 kPa. What is the composition of the distillate?

[Solution](#)

- 6.15.** Calculate the composition of the vapor in equilibrium at 323 K with a liquid solution of 0.600 mol fraction 2-methyl-1-propanol (isobutyl alcohol) and 0.400 mol fraction 3-methyl-1-butanol (isoamyl alcohol). The vapor pressure of pure isobutyl alcohol is 7.46 kPa and that of pure isoamyl alcohol is 2.33 kPa both at 323 K.

[Solution](#)

**6.16.** The thermal expansion coefficient  $\alpha = (1/V) (\partial V/\partial T)_p$  is often used when predicting changes in vapor pressure induced by temperature changes. From the relation  $\rho = m/V$ , show that  $\alpha = -(\partial \ln \rho / \partial T)_p$ .

[Solution](#)

**6.17.** At 293.15 K the density of water is 0.998 234 g cm<sup>-3</sup> and at 294.15 K it is 0.998 022 g cm<sup>-3</sup> under 1 atm of pressure. Estimate the value of  $\alpha$  for water at 1 atm.

[Solution](#)

**6.18.** How many theoretical plates are required to separate the mixture shown in Fig. 6.7?

[Solution](#)

**\*6.19.** A sealed reaction vessel is completely filled with liquid water at 293.15 K and 1.00 atm. If the temperature is raised exactly 6 K and the walls of the vessel remain rigid, what is the pressure in the container if the average value of  $\alpha = 2.85 \times 10^{-4} \text{ K}^{-1}$  and the compressibility coefficient  $\kappa = -(1/V)(\partial V/\partial P)_T$  is  $4.49 \times 10^{-5} \text{ atm}^{-1}$ ?

[Solution](#)

### Construction of Phase Diagrams from Physical Data

**6.20.** In Figure 6.16, a solution having composition  $p$  is cooled to just above the eutectic temperature (point  $s$  is about 0.18  $x_{\text{Si}}$ , and  $x_e$  is 0.31  $x_{\text{Si}}$ ); calculate the composition of the solid that separates and that of the liquid that remains.

[Solution](#)

**\*6.21.** The melting points and heats of fusion of gold and silicon are

	Au	Si
$T/\text{K}$	1337	1683
$\Delta_{\text{fus}} H/\text{J mol}^{-1}$	12 677.5	39 622.5

For the data, calculate the solid-liquid equilibrium lines and estimate the eutectic composition graphically. Compare the result with the values given by Figure 6.16.

[Solution](#)

**6.22.** Use the following data to construct a phase diagram of the phenol–water system and answer the following questions (the compositions are given in grams of phenol in 100 grams of solution):

$t/^{\circ}\text{C}$	20	25	30	35	40	
Aqueous layer	8.40	8.71	8.92	9.34	9.78	
Phenol layer	72.24	71.38	69.95	68.28	66.81	
	45	50	55	60	65	68.8
	10.62	12.08	13.88	17.10	22.26	35.90
	65.02	62.83	60.18	56.10	49.34	35.90

- What will be the compositions of the layers formed from a solution of 30 g phenol and 70 g water maintained at 30 °C?
- A solution of 20 g phenol and 80 g water is prepared at 70 °C. How many phases will be present?
- At what temperature will two phases appear if the solution in part (b) is cooled gradually? What will be the compositions of the two phases?

[Solution](#)

- 6.23.** The following information is obtained from cooling curve data on the partial system  $\text{Fe}_2\text{O}_3\text{--Y}_2\text{O}_3$  [J. W. Nielsen and E. F. Dearborn, *Phys. Chem. Solids*, 5, 203(1958)]:

Composition of Melt/mol % $\text{Y}_2\text{O}_3$	Temperature of Break/ $^{\circ}\text{C}$	Temperature of Halt/ $^{\circ}\text{C}$
0		1550
5	1540	1440
10	1515	1440
15	1450	1440
20	1520	1440
25	1560	1440
30	1620	1575/1440
40	1705	1575
50		1720

Sketch the simplest melting point diagram consistent with these data. Label the phase regions and give the composition of any compounds formed.

[Solution](#)

- 6.24.** The study of cooling curves for the thallium–gold system yields the following data. Construct the phase diagram and identify the eutectic composition and temperature. Pure gold melts at  $1063^{\circ}\text{C}$  and pure thallium melts at  $302^{\circ}\text{C}$ . In each region, identify the number of phases and the solid that separates out, if any.

Wt % Au	10	20	30	40	60	80	90
First break ( $^{\circ}\text{C}$ )	272	204	200	400	686	910	998
Eutectic halt ( $^{\circ}\text{C}$ )	128	128	128	128	128	128	128

[Data adapted from A. C. K. Smith, *Applied Physical Chemistry Problems*, London: McGraw-Hill, 1968, p. 13.]

[Solution](#)



- 6.25. a.** From the following information, draw the binary phase diagram for the system FeO (mp. 1370 °C)–MnO (mp. 1785 °C). A peritectic reaction occurs at 1430 °C between  $\alpha$  solid solution containing 30 mass % MnO and solid solution containing 60 mass % MnO. These are in equilibrium with melt that contains 15 mass % MnO. At 1200 °C the composition of  $\alpha$  and  $\beta$  solution is 28 mass % and 63 mass %, respectively.

**b.** Describe what happens as a liquid containing 28 mass % MnO is cooled to 1200 °C.

[Solution](#)

- 6.26.** The following data for the magnesium–copper system is the result of analyzing cooling curves. Pure copper melts at 1085 °C while pure magnesium melts at 659 °C. Two compounds are formed, one at 16.05 wt % Mg with a melting point of 800 °C, and the other at 43.44 wt % Mg with a melting point of 583 °C, respectively. Construct the phase diagram from this information and identify the compositions of the eutectics. [Data adapted from A. C. K. Smith, *Applied Physical Chemistry Problems*, London: McGraw-Hill, 1968, p. 14.]

Wt % Mg	5	10	15	20	30	35		
First break (°C)	900	702	785	765	636	565		
Eutectic halt (°C)	680	680	680	560	560	560		
	40	45	50	60	70	80	90	
	581	575	546	448	423	525	600	
	560	360	360	360	360	360	360	

[Solution](#)

- 6.27.** What are the empirical formulae of the compounds represented by the vertical lines formed in the magnesium–copper system described in Problem 6.26?

[Solution](#)



- 6.28.** A preliminary thermal analysis of the Fe–Au system showed two solid phases of composition 8.1 mol % Au and 25.5 mol % Au in equilibrium at 1168 °C with liquid of composition 43 mol % Au. Construct the simplest melting point diagram consistent with this information and label all the phase regions. Sketch the cooling curves for the composition 10 mol % Au, 30 mol % A, and 60 mol % Au, and make them consistent with the fact that there is an  $\alpha$ - $\gamma$  phase transition in iron at 903 °C and that the  $\gamma$ -phase field extends to 45 mol % Au at this temperature. Iron melts at 1536 °C and gold at 1063 °C.

[Solution](#)

- 6.29.** The aluminum–selenium system was determined from thermal analysis.  $\text{Al}_2\text{Se}_3$  melts congruently at approximately 950 °C and forms a eutectic both with aluminum and with selenium at a very low concentration of the alloying element and at a temperature close to the melting point of the base elements. Draw a diagram from this information and give the composition of the phases. Aluminum melts at 659.7 °C and selenium melts at approximately 217 °C.

[Solution](#)

- \*6.30.** The metals Al and Ca form the compounds  $\text{Al}_4\text{Ca}$  and  $\text{Al}_2\text{Ca}$ . The solids Al, Ca,  $\text{Al}_4\text{Ca}$ , and  $\text{Al}_2\text{Ca}$  essentially are immiscible in each other but are completely miscible as liquids. Maximum Ca solubility in Al is about 2% and occurs at 616 °C. Al melts at 659.7 °C and Ca melts at 848 °C. Compound  $\text{Al}_2\text{Ca}$  melts congruently at 1079 °C and gives a simple eutectic with Ca at 545°C. Compound  $\text{Al}_4\text{Ca}$  decomposes at 700 °C to give  $\text{Al}_2\text{Ca}$  and a melt, the peritectic lying at 10 mol %. A monotectic exists at 616 °C. At approximately 450 °C a transition occurs between  $\alpha$ -Ca and  $\beta$ -Ca.

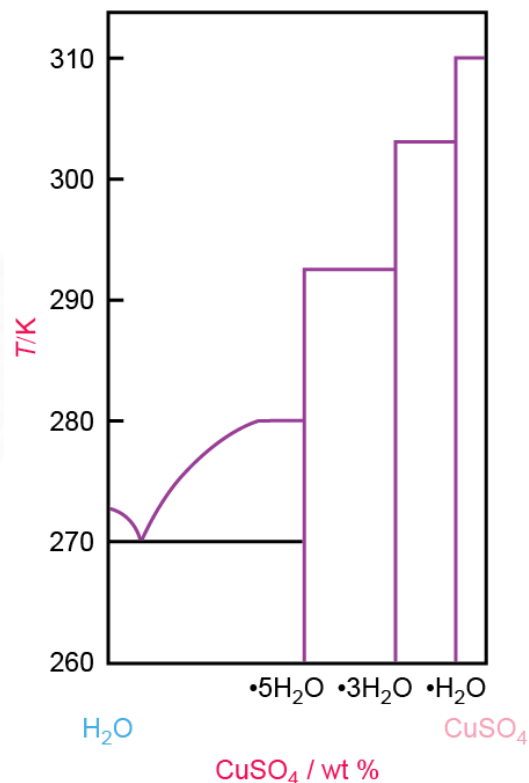
- a. Draw the simplest phase diagram consistent with this information and label all phase regions.
- b. Sketch cooling curves for melts of composition 15 mol % Ca and 80 mol % Ca.

[Solution](#)

**\*6.31.** The extent of dehydration of a salt such as  $\text{CuSO}_4$  can often be followed by measuring the vapor pressure over the hydrated salt. The system  $\text{H}_2\text{O}$ – $\text{CuSO}_4$  is shown in the accompanying figure as an example of such a system. Label the areas as to the phase(s) present. Then describe the sequence of phase changes if a dilute solution of copper sulfate is dehydrated at 275 K, ending with anhydrous copper sulfate. What would a vacuum gauge read starting with pure water during the dehydration process at 298.15 K? Sketch a plot of  $P/\text{Torr}$  against  $\text{CuSO}_4/\text{wt } \%$ . Relevant data are:

The Vapor Pressure of  $\text{CuSO}_4\text{--H}_2\text{O}$  at 298.15 K

	$P/\text{Torr}$
Vapor + saturated solution + $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	16
Vapor $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$	7.85
Vapor + $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ + $\text{CuSO}_4 \cdot \text{H}_2\text{O}$	4.32
Vapor + $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ + $\text{CuSO}_4$	0.017
Vapor pressure of water	23.8



[Solution](#)

- \*6.32.** The data in the accompanying table are approximate for the isobaric-isothermal system  $\text{SnO}_2$ – $\text{CaO}$ – $\text{MgO}$  at 298.15 K and 1 atm. Sketch a reasonable phase diagram in mol % with  $\text{SnO}_2$  at the apex of the triangle. Label all phase regions; the results are known as composition triangles.

Material	In Equilibrium with Solid Phases
$\text{SnO}_2$	$(\text{MgO})_2\text{SnO}_2$ , $\text{CaOSnO}_2$
$(\text{MgO})_2\text{SnO}_2$	$\text{SnO}_2$ , $(\text{CaO})\text{SnO}_2$ , $\text{MgO}$
$\text{MgO}$	$\text{CaO}$ , $(\text{CaO})_2\text{SnO}_2$
$\text{CaO}$	$\text{MgO}$ , $(\text{CaO})_2\text{SnO}_2$
$(\text{CaO})_2\text{SnO}_2$	$\text{CaO}$ , $\text{MgO}$ , $\text{CaOSnO}_2$
$\text{CaOSnO}_2$	$(\text{CaO})_2\text{SnO}_2$ , $\text{MgO}$ , $(\text{MgO})_2\text{SnO}_2$ , $\text{SnO}_2$

[Solution](#)

- 6.33.** Sketch the  $P$  against  $T$  diagram for phosphorous from the following information. White phosphorous melts at 311 K and 0.2 Torr; red phosphorous melts at 763 K and 43 atm. The white form is more dense than the liquid and the red form is less dense than the liquid. The vapor pressure of the white form is everywhere greater than that of the red form. Label each area on the plot, and explain which triple point(s) is (are) stable or metastable.

[Solution](#)

- 6.34.** Giguère and Turrell, *J. Am. Chem. Soc.*, 102, 5476(1980), describe three ionic hydrates formed between HF and  $\text{H}_2\text{O}$ . Sketch the  $\text{H}_2\text{O}$ –HF phase diagram in mol % HF from the following information.  $\text{HF} \cdot \text{H}_2\text{O}$  melts at  $-35.2^\circ\text{C}$ ,  $2\text{HF} \cdot \text{H}_2\text{O}$  decomposes by a peritectic reaction at  $-75^\circ\text{C}$ , and  $4\text{HF} \cdot \text{H}_2\text{O}$  melts at  $-98.2^\circ\text{C}$ . HF melts at  $-83.1^\circ\text{C}$ . Label the composition of all regions. The eutectic occurs at  $-111^\circ\text{C}$  with monotectics at  $-71^\circ\text{C}$ ,  $-77^\circ\text{C}$ , and  $-102^\circ\text{C}$ .

[Solution](#)

- 6.35.** In the system A–B a line of three-phase equilibrium occurs at 900 K as determined by thermal analysis. A second three-phase equilibrium occurs at 500 K. Only one halt is observed for any one cooling curve. The compound  $\text{AB}_2$  is known and melts at 600 K. If A melts at 1200 K and B at 700 K, sketch the simplest phase diagram consistent with the given data. Label each region.

[Solution](#)

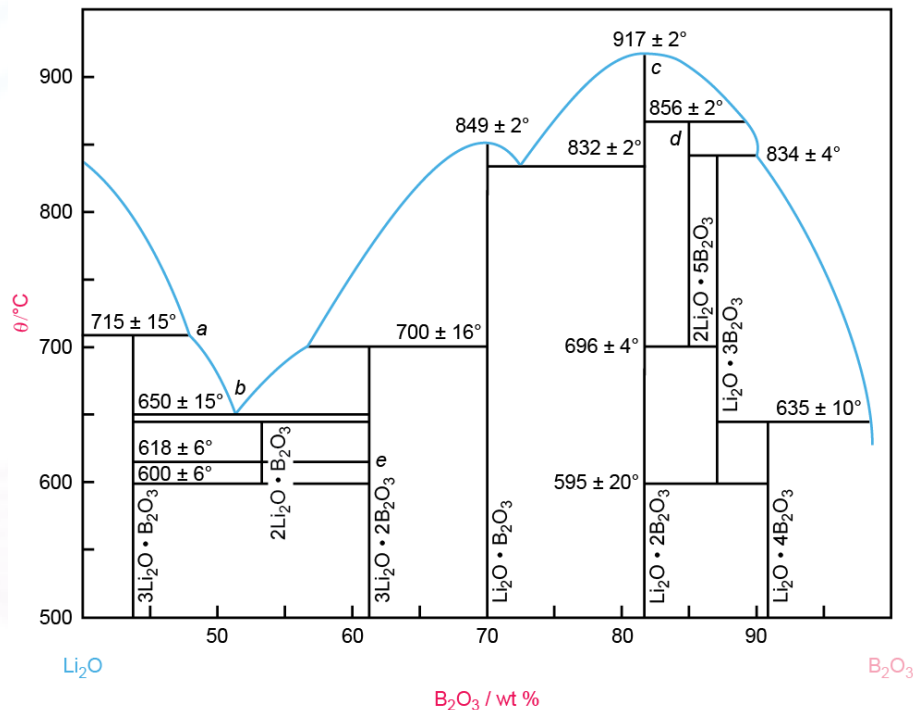
## Data Derived from Phase Diagrams of Condensed Systems

**6.36.** The following questions refer to Figure 6.28:

- If liquid C were added to the system, what changes would occur if the system originally contained 80% salt A and 20% salt B?
- What changes would occur if the system originally contained 50% salt A and 50% salt B upon the addition of liquid?
- If liquid is added to an unsaturated solution of salt A and salt B in solution of composition lying at *e*, what changes would occur?

[Solution](#)

**6.37.** In the accompanying diagram, due to B. S. R. Sastry and F. A. Hammel, *J. Am. Ceramic Soc.*, 42; 218(1959), identify the composition of all the areas. Identify the phenomenon associated with each lettered position.



[[Diagram for Problem 6.37. Reprinted with permission of The American Ceramic Society, Post Office Box 6136, Westerville, OH 43086-6136, Copyright © 1964 by the American Ceramic Society. All rights reserved.]]

[Solution](#)

- 6.38.** Describe what happens within the system  $\text{Mn}_2\text{O}_3\text{--Al}_2\text{O}_3$  in Fig. 6.21 when a liquid of  $x_{\text{Al}_2\text{O}_3} = 0.2$  is cooled from 2100 K to 1200 K.

[Solution](#)

- 6.39.** The isobaric solubility diagram for the system acetic acid–toluene–water is shown in Figure 6.27. What phase(s) and their composition(s) will be present if 0.2 mol of toluene is added to a system consisting of 0.5 mol of water and 0.3 mol of acetic acid? Give the relative amounts of each phase.

[Solution](#)

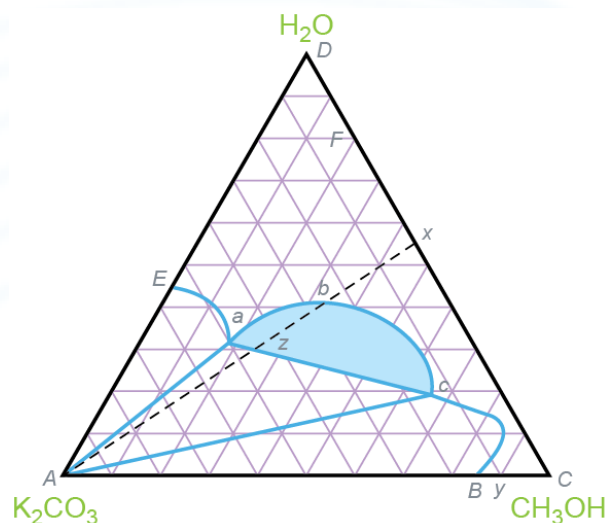
- 6.40.** A fictitious ternary system composed of liquids A, B, and C was constructed by adding the component B to various binary A–C mixtures and noting the point at which complete miscibility occurred. The following are the mole-percents of A and B at which complete miscibility was observed. Construct the phase diagram on a triangular graph paper.

$x_{\text{A}}(\%)$	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0
$x_{\text{B}}(\%)$	20.0	27.0	30.0	28.0	26.0	22.0	17.0	12.0	7.0

Comment on the variation of the mutual solubility of A and C as B is added.

[Solution](#)

**6.41.** In organic chemistry it is a common procedure to separate a mixture of an organic liquid in water by adding a salt to it. This is known as “salting out.” The ternary system  $\text{K}_2\text{CO}_3\text{--H}_2\text{O--CH}_3\text{OH}$  is typical. The system is distinguished by the appearance of the two-liquid region *abc*.



- Describe the phase(s) present in each region of the diagram.
- What would occur as solid  $\text{K}_2\text{CO}_3$  is added to a solution of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  of composition  $x$ ?
- How can the organic-rich phase in (b) be separated?
- How can  $\text{K}_2\text{CO}_3$  be precipitated from a solution having composition  $y$ ?
- Describe in detail the sequence of events when a solution of composition  $F$  is evaporated.

### Solution



**Essay Questions**

- 6.42.** How is thermal analysis used to determine the liquid-solid equilibria and the eutectic temperature?
- 6.43.** Explain what is meant by a *metastable system*.
- 6.44.** Outline how isothermal distillation may be used to prepare a pure sample.
- 6.45.** Detail the process by which a pure sample is obtained using a fractionating column.
- 6.46.** What is the difference on a molecular level between a maximum and minimum boiling azeotrope? How do the plots of  $P$  against  $x$  and  $T$  against  $x$  differ?
- 6.47.** How would you distinguish between an azeotrope and a pure compound?
- 6.48.** A synthetic chemist has prepared several zwitterionic compounds in a homogeneous series. With each compound a reproducible melting point is determined using different samples from a fresh batch of material. If, however, the same sample is used in repeating the determination, a progressively lower melting-point temperature is obtained. Explain what is happening.

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**Solutions**

**6.1.** In Figure 6.1, in the region marked *orthorhombic*, how many degrees of freedom exist? How many components are present? How many phases? How many phases exist in the region marked *monoclinic*?

**Solution:**

The region marked *orthorhombic* is a single phase region. Since this is the phase diagram for pure sulfur, there is only one component. From the phase rule, given by Eq. 6.2,  $f = c - p + 2$ , with  $c = 1$  and  $p = 1$ ,  $f = 1 - 1 + 2 = 2$ . The two degrees of freedom are pressure and temperature.

There is only one phase in the region marked *monoclinic*.

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**6.2.** What is the composition of the two-phase region in Figure 6.14? How many degrees of freedom exist in this region?

**Solution:**

The compositions of the two phases at a particular temperature are:

- i. Water saturated with nicotine
- ii. Nicotine saturated with water

The number of degrees of freedom is given by Eq . 6.2,

$$f = c - p + 2$$

$$f = 2 - 2 + 2$$

$$\boxed{f = 2}$$

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**6.3.** Determine the number of degrees of freedom for the following systems:

- a. A solution of potassium chloride in water at the equilibrium pressure.
- b. A solution of potassium chloride and sodium chloride at 298 K at 1 atm pressure.
- c. Ice in a solution of water and alcohol.

**Solution:**

The number of degrees of freedom is given by Eq. 6.2,

$$f = c - p + 2$$

a. For KCl solution,  $c = 2$  since it completely dissociates into two ions in water, and  $p = 1$  since there is only one phase.

$$f = 2 - 1 + 2$$

$$f = 3$$

However, since equilibrium pressure has been specified, the degrees of freedom drops by one, and

$$\boxed{f = 2}$$

b. For KCl and NaCl solution,  $c = 3$  since there are three ions present,  $K^+$ ,  $Cl^-$  and  $Na^+$ , and  $p = 1$  since there is only one phase.

$$f = 3 - 1 + 2$$

$$f = 4$$

However, since the restriction of constant pressure has been specified, the degrees of freedom drops by one, and

$$\boxed{f = 3}$$

c. For ice, water and alcohol,  $c = 2$  since water and ice are considered one component.  $p = 2$  since there is a solid and a liquid phase.

$$f = 2 - 2 + 2$$

$$\boxed{f = 2}$$

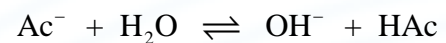
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**6.4.** How many components are present in a water solution of sodium acetate?

**Solution:**

The system is given by



Aqueous sodium acetate is a two-component system even though the above hydrolysis takes place, since the equilibrium constant defines the concentration of  $\text{OH}^-$  and  $\text{HAc}$  if the concentration of sodium acetate is given.

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**6.5.** How many components are present in the system  $\text{CaCO}_3\text{--CaO--CO}_2$ ?

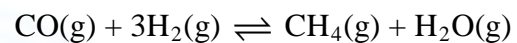
**Solution:**

There are three components in the system  $\text{CaCO}_3\text{--CaO--CO}_2$ . However, since a chemical reaction can take place in the given system, the number of components is reduced by the number of equilibrium conditions, in this case 1. Therefore  $\boxed{c = 2}$ .

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**6.6.** How many components are present in the following system?



**Solution:**

There are four different gases, or components in the above system. However, since a chemical reaction can take place in the given system, the number of components is reduced by the number of equilibrium conditions, in this case 1. Therefore  $\boxed{c = 3}$ .

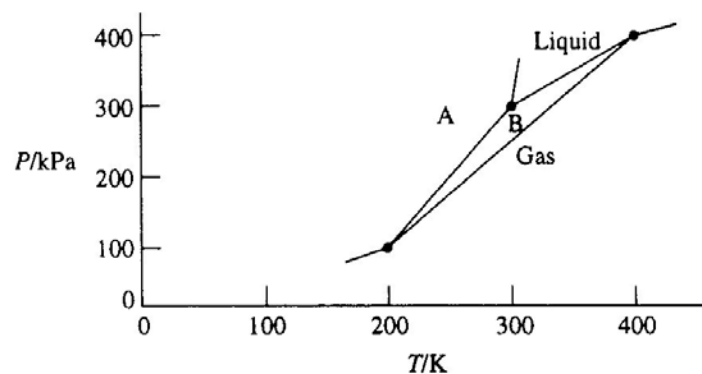
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- 6.7.** A certain substance exists in two solid phases A and B and also in the liquid and gaseous states. Construct a  $P$ - $T$  phase diagram indicating the regions of stable existence for each phase from the following triple-point data:

T/K	P/kPa	Phase in Equilibrium
200	100	A, B, gas
300	300	A, B, liquid
400	400	B, liquid, gas

**Solution:**

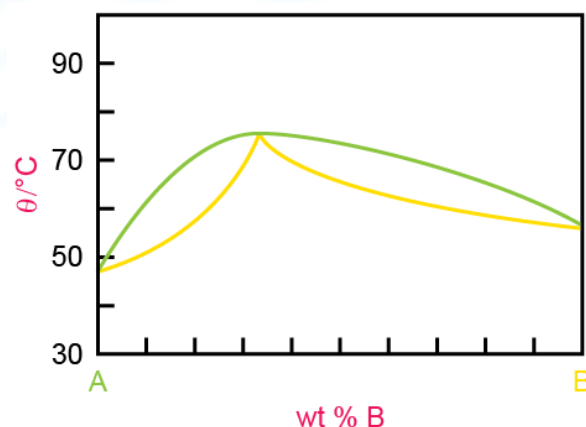


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**6.8.** Answer the following questions, using the accompanying figure.

- A liquid mixture consists of 33 g of component A and 99 g of component B. At what temperature would the mixture begin to boil?
- Under the conditions in (a), what is the composition of the vapor when boiling first occurs?
- If the distillation is continued until the boiling point is raised by 5.0 °C, what would be the composition of the liquid left in the still?



- Under the conditions in (c), what are the composition and mass of the two components collected over the initial 5.0 °C interval?

**Solution:**

- To calculate the temperature at which the mixture would begin to boil, we need to find the weight percent of the component B.

$$\text{weight \% B} = \frac{m_B}{m_A + m_B} \times 100\%$$

$$\text{weight \% B} = \frac{99 \text{ g}}{33 \text{ g} + 99 \text{ g}} \times 100\%$$

$$\text{weight \% B} = 75\%$$

The temperature corresponding to 75% B is approximately 60 °C, where the mixture first begins to boil.



$$T \approx 60^\circ\text{C}$$

b. The composition of the vapor is given by the intersection of the tie line at the vapor curve. In this case, the vapor has a composition of approximately 88% B

$$\text{weight \% B} \approx 88\%$$

c. The boiling temperature becomes  $65.0^\circ\text{C}$ . The composition of the vapor is approximately 53% B

$$\text{weight \% B} \approx 53\%$$

d. using the average composition of the distillates as the value halfway between the initial and final composition of the distillates, we obtain,

$$\text{weight \% B} = \frac{1}{2}(88\% + 70\%)$$

$$\text{weight \% B} = 79\%$$

Let  $W_R$  = mass of residue and  $W_D$  = mass of distillate

$$W_{\text{total}} = W_R + W_D = 132 \text{ g}$$

Then, applying the condition that B is distributed through the residue and distillate, we obtain

$$m_{\text{B in residue}} + m_{\text{B in distillate}} = 99 \text{ g}$$

$$0.53W_{\text{R}} + 0.79W_{\text{D}} = 99 \text{ g}$$

$$0.53(132 \text{ g} - W_{\text{D}}) + 0.79W_{\text{D}} = 99 \text{ g}$$

$$69.96 \text{ g} - 0.53W_{\text{D}} + 0.79W_{\text{D}} = 99 \text{ g}$$

$$69.96 \text{ g} + 0.26W_{\text{D}} = 99 \text{ g}$$

$$W_{\text{D}} = \frac{99 \text{ g} - 69.96 \text{ g}}{0.26}$$

$$W_{\text{D}} = 111.692\,307\,7 \text{ g}$$

$$W_{\text{R}} = 132 \text{ g} - 111.692\,307\,7 \text{ g}$$

$$W_{\text{R}} = 20.307\,692\,31 \text{ g}$$

The distillate is therefore 79% of the value of  $W_{\text{D}}$ ,

$$m_{\text{B in distillate}} = 0.79W_{\text{D}}$$

$$m_{\text{B in distillate}} = 0.79(111.692\,307\,7 \text{ g})$$

$$m_{\text{B in distillate}} = 88.236\,923\,08 \text{ g}$$

$$\boxed{m_{\text{B in distillate}} = 88.2 \text{ g}}$$

$$m_{\text{A in distillate}} = 111.692\,307\,7 \text{ g} - 88.236\,923\,08 \text{ g}$$

$$m_{\text{A in distillate}} = 23.455\,384\,62 \text{ g}$$

$$\boxed{m_{\text{A in distillate}} = 23.5 \text{ g}}$$

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- 6.9.** From the data of Figure 6.14, calculate the ratio of the mass of the water-rich layer to that of the nicotine-rich layer, for a 40 wt % water–nicotine mixture at 350 K.

**Solution:**

Given: Figure 6.14, 40wt % water – nicotine,  $T = 350$  K

Required:  $\frac{m_{\text{water}}}{m_{\text{nicotine}}}$

From Figure 6.14, the composition at 350 K at equilibrium between the single-phase water-rich layer and the two-phase region is approximately 10% nicotine. For the equilibrium value on the nicotine-rich side, the value is approximately 75% nicotine.

Using the lever rule, given by Eq. 6.16, we can solve for the ratio,

$$\frac{n_1}{n_v} = \frac{y_1 - x_T}{x_T - x_1} = \frac{pv}{lp}$$

$$\frac{m_{\text{water}}}{m_{\text{nicotine}}} = \frac{75 - 40}{40 - 10}$$

$$\frac{m_{\text{water}}}{m_{\text{nicotine}}} = \frac{35}{30}$$

$$\frac{m_{\text{water}}}{m_{\text{nicotine}}} = 1.166\ 666\ 667$$

$$\boxed{\frac{m_{\text{water}}}{m_{\text{nicotine}}} = 1.2}$$

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**6.10.** The ratio of the mass of chlorobenzene to that of water collected in a steam distillation is 1.93 when the mixture was boiled at 343.85 K and 56.434 kPa. If the vapor pressure of water at this temperature is 43.102 kPa, calculate the molar mass of chlorobenzene.

**Solution:**

Given:  $\frac{m_{\text{chlorobenzene}}}{m_{\text{water}}} = 1.93$ ,  $T = 343.85 \text{ K}$ ,  $P = 56.434 \text{ kPa}$ ,  $P_{\text{water}} = 43.102 \text{ kPa}$

Required:  $M_{\text{chlorobenzene}}$

Using Eq. 6.21,

$$\frac{n_A}{n_B} = \frac{P_A^*}{P_B^*}$$

Using,  $n = \frac{m}{M}$  we can rearrange and solve for  $M_{\text{chlorobenzene}}$ ,

$$\frac{m_{\text{chlorobenzene}} M_{\text{water}}}{m_{\text{water}} M_{\text{chlorobenzene}}} = \frac{P_{\text{chlorobenzene}}^*}{P_{\text{water}}^*}$$

$$M_{\text{chlorobenzene}} = \frac{m_{\text{chlorobenzene}} M_{\text{water}}}{m_{\text{water}}} \frac{P_{\text{water}}^*}{P_{\text{chlorobenzene}}^*}$$

$$M_{\text{water}} = 2(1.00794 \text{ g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_{\text{water}} = 18.01528 \text{ g mol}^{-1}$$

The vapor pressure of pure chlorobenzene is obtained using Dalton's law of partial pressures,

$$P_{\text{chlorobenzene}}^* = P - P_{\text{water}}^*$$

$$P_{\text{chlorobenzene}}^* = 56.434 \text{ kPa} - 43.102 \text{ kPa}$$

$$P_{\text{chlorobenzene}}^* = 13.332 \text{ kPa}$$

$$M_{\text{chlorobenzene}} = 1.93(18.01528 \text{ g mol}^{-1}) \frac{43.102 \text{ kPa}}{13.332 \text{ kPa}}$$

$$M_{\text{chlorobenzene}} = 112.408834 \text{ g mol}^{-1}$$

$$M_{\text{chlorobenzene}} = 112.41 \text{ g mol}^{-1}$$

The actual molar mass of chlorobenzene,  $\text{C}_6\text{H}_5\text{Cl}$  is

$$M_{\text{chlorobenzene}} = 6(12.011 \text{ g mol}^{-1}) + 5(1.00794 \text{ g mol}^{-1}) + (35.4527 \text{ g mol}^{-1})$$

$$M_{\text{chlorobenzene}} = 112.5584 \text{ g mol}^{-1}$$

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**6.11. a.** Do the actual derivation of Eq. 6.11 from Eq. 6.8.

**b.** From Eq. 6.8 derive an expression that gives you the ratio of the mass of two volatile components, 1 and 2, in terms of their mole fractions in the vapor and their molar masses.

**Solution:**

**a.** Equation 6.11 is given by

$$P = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*) y_1}$$

We can manipulate Eq. 6.8 to obtain the same result.

$$y_1 = \frac{P_1}{P}$$

The total pressure is given by the sum of partial pressures of each of the components in a mixture, hence,

$$P = P_1 + P_2$$

Raoult's Law is given by Eq. 5.26, therefore we can use it solve for  $P$

$$P_1 = x_1 P_1^*; \quad P_2 = x_2 P_2^*$$

$$P = P_1 + P_2$$

$$P = x_1 P_1^* + x_2 P_2^*$$

$$P = x_1 P_1^* + (1 - x_1) P_2^*$$

$$P = x_1 P_1^* + P_2^* - x_1 P_2^*$$

$$P = (P_1^* - P_2^*) x_1 + P_2^*$$

**b.** Using Eq. 6.8, we can obtain an expression for  $x_1$ ,

$$y_1 = \frac{P_1}{P}$$

$$y_1 = \frac{x_1 P_1^*}{P_2^* + x_1 (P_1^* - P_2^*)}$$

Solving for  $x_1$  gives

$$x_1 P_1^* = y_1 P_2^* + y_1 x_1 (P_1^* - P_2^*)$$

$$x_1 [P_1^* - y_1 (P_1^* - P_2^*)] = y_1 P_2^*$$

$$x_1 = \frac{y_1 P_2^*}{P_1^* - y_1 (P_1^* - P_2^*)}$$

This expression may now be substituted back into Eq. 6.9 with the elimination of  $x_1$ . The result is

$$P = (P_1^* - P_2^*) \frac{y_1 P_2^*}{y_1 (P_1^* - P_2^*) - P_1^*} + P_2^*$$

$$P = \frac{y_1 P_2^* (P_1^* - P_2^*) + P_2^* (y_1 (P_1^* - P_2^*) - P_1^*)}{y_1 (P_1^* - P_2^*) - P_1^*}$$

$$P = \frac{\cancel{y_1 P_2^* (P_1^* - P_2^*)} + y_1 P_2^* (\cancel{P_1^* - P_2^*}) - P_1^* P_2^*}{y_1 (P_1^* - P_2^*) - P_1^*}$$

$$P = \frac{-P_1^* P_2^*}{y_1 (P_1^* - P_2^*) - P_1^*}$$

Multiplying by  $\frac{-1}{-1}$  to remove the negative sign, we obtain,

$$P = \frac{P_1^* P_2^*}{P_1^* - y_1 (P_1^* - P_2^*)}$$

Which is the same equation as Eq. 6.11.

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**6.12.** Obtain an expression for the ratio of masses of the materials distilled in a steam distillation in terms of the molar masses and the partial pressures of the two components.

**Solution:**

To solve this problem, we can use the expression for the composition of vapor, given by Eq. 6.21,

$$\frac{n_A}{n_B} = \frac{P_A^*}{P_B^*}$$

Using,  $n = \frac{m}{M}$  we can rearrange and solve for the masses of the materials distilled

$$\frac{m_A M_B}{m_B M_A} = \frac{P_A^*}{P_B^*}$$

$$\frac{m_A}{m_B} = \frac{P_A^* M_A}{P_B^* M_B}$$

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**6.13.** Under atmospheric pressure 1 kg of pure naphthalene is to be prepared by steam distillation at 372.4 K. What mass of steam is required to perform this purification? The vapor pressure of pure water at 372.4 K is 98.805 kPa.

**Solution:**

Given:  $P = 101.325 \text{ kPa}$ ,  $m_{\text{naphthalene}} = 1 \text{ kg}$ ,  $T = 372.4 \text{ K}$ ,  $P_{\text{water}}^* = 98.805 \text{ kPa}$

Required:  $m_{\text{steam}}$

To solve this problem, we can use the expression for the composition of vapor, given by Eq. 6.21,

$$\frac{n_A}{n_B} = \frac{P_A^*}{P_B^*}$$

Using,  $n = \frac{m}{M}$  we can rearrange and solve for the masses of the materials distilled

$$\frac{m_A M_B}{m_B M_A} = \frac{P_A^*}{P_B^*}$$

$$\frac{m_A}{m_B} = \frac{P_A^* M_A}{P_B^* M_B}$$

$$m_{\text{steam}} = \frac{P_{\text{steam}}^* M_{\text{steam}} m_{\text{naphthalene}}}{P_{\text{naphthalene}}^* M_{\text{naphthalene}}}$$

The vapor pressure of pure naphthalene is obtained using Dalton's law of partial pressures,

$$P_{\text{naphthalene}}^* = P - P_{\text{water}}^*$$

$$P_{\text{naphthalene}}^* = 101.325 \text{ kPa} - 98.805 \text{ kPa}$$

$$P_{\text{naphthalene}}^* = 2.52 \text{ kPa}$$

$$M_{\text{steam}} = M_{\text{H}_2\text{O}} = 2(1.00794 \text{ g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_{\text{steam}} = 18.01528 \text{ g mol}^{-1}$$

The formula for naphthalene is  $\text{C}_{10}\text{H}_8$ , therefore the molar mass is

$$M_{\text{naphthalene}} = 10(12.011 \text{ g mol}^{-1}) + 8(1.00794 \text{ g mol}^{-1})$$

$$M_{\text{naphthalene}} = 128.17352 \text{ g mol}^{-1}$$

Solving for the mass of steam, we obtain

$$m_{\text{steam}} = \frac{(98.805 \text{ kPa})(18.01528 \text{ g mol}^{-1})(1 \text{ kg})}{(2.52 \text{ kPa})(128.17352 \text{ g mol}^{-1})}$$

$$m_{\text{steam}} = 5.510809449 \text{ kg}$$

$$m_{\text{steam}} = 5.5108 \text{ kg}$$

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**6.14.** The vapor pressure of water at 343.85 K is 43.102 kPa. A certain mixture of chlorobenzene and water boils at 343.85 K under a reduced pressure of 56.434 kPa. What is the composition of the distillate?

**Solution:**

Given:  $T = 343.85 \text{ K}$ ,  $P_{\text{water}}^* = 43.102 \text{ kPa}$ ,  $P = 56.434 \text{ kPa}$

Required:  $\frac{m_{\text{chlorobenzene}}}{m_{\text{water}}}$

To solve this problem, we can use the expression for the composition of vapor, given by Eq. 6.21,

$$\frac{n_A}{n_B} = \frac{P_A^*}{P_B^*}$$

Using,  $n = \frac{m}{M}$  we can rearrange and solve for the masses of the materials distilled

$$\frac{m_A M_B}{m_B M_A} = \frac{P_A^*}{P_B^*}$$

$$\frac{m_A}{m_B} = \frac{P_A^* M_A}{P_B^* M_B}$$

$$\frac{m_{\text{chlorobenzene}}}{m_{\text{water}}} = \frac{P_{\text{chlorobenzene}}^* M_{\text{chlorobenzene}}}{P_{\text{water}}^* M_{\text{water}}}$$

The vapor pressure of pure chlorobenzene is obtained using Dalton's law of partial pressures,

$$P_{\text{chlorobenzene}}^* = P - P_{\text{water}}^*$$

$$P_{\text{chlorobenzene}}^* = 56.434 \text{ kPa} - 43.102 \text{ kPa}$$

$$P_{\text{chlorobenzene}}^* = 13.332 \text{ kPa}$$

The formula for chlorobenzene is  $\text{C}_6\text{H}_5\text{Cl}$  therefore the molar mass is

$$M_{\text{chlorobenzene}} = 6(12.011 \text{ g mol}^{-1}) + 5(1.007 \text{ 94 g mol}^{-1}) + (35.4527 \text{ g mol}^{-1})$$

$$M_{\text{chlorobenzene}} = 112.5584 \text{ g mol}^{-1}$$

$$M_{\text{water}} = 2(1.007 \text{ 94 g mol}^{-1}) + (15.9994 \text{ g mol}^{-1})$$

$$M_{\text{water}} = 18.015 \text{ 28 g mol}^{-1}$$

$$\frac{m_{\text{chlorobenzene}}}{m_{\text{water}}} = \frac{(13.332 \text{ kPa})(112.5584 \text{ g mol}^{-1})}{(43.102 \text{ kPa})(18.015 \text{ 28 g mol}^{-1})}$$

$$\frac{m_{\text{chlorobenzene}}}{m_{\text{water}}} = 1.932 \text{ 567 968}$$

$\frac{m_{\text{chlorobenzene}}}{m_{\text{water}}} = 1.9326$
--

The sample contains 1.9326 g of chlorobenzene for each 1.000 g of water.

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**6.15.** Calculate the composition of the vapor in equilibrium at 323 K with a liquid solution of 0.600 mol fraction 2-methyl-1-propanol (isobutyl alcohol) and 0.400 mol fraction 3-methyl-1-butanol (isoamyl alcohol). The vapor pressure of pure isobutyl alcohol is 7.46 kPa and that of pure isoamyl alcohol is 2.33 kPa both at 323 K.

**Solution:**

Given:  $T = 323 \text{ K}$ ,  $x_{\text{isobutyl alcohol}} = 0.600$ ,  $x_{\text{isoamyl alcohol}} = 0.400$ ,  $P_{\text{isobutyl alcohol}}^* = 7.46 \text{ kPa}$ ,  $P_{\text{isoamyl alcohol}}^* = 2.33 \text{ kPa}$

Required:  $y_{\text{isoamyl alcohol}}$ ,  $y_{\text{isobutyl alcohol}}$

To determine the composition of the vapor in equilibrium, we can use Eq. 6.18,

$$y_1 = \frac{x_1 P_1^*}{x_1 P_1^* + x_2 P_2^*}$$

$$y_a = \frac{x_a P_a^*}{x_a P_a^* + x_b P_b^*}$$

$$y_a = \frac{(0.600)(7.46 \text{ kPa})}{(0.600)(7.46 \text{ kPa}) + (0.400)(2.33 \text{ kPa})}$$

$$y_a = 0.827 \ 662 \ 721 \ 9$$

$$\boxed{y_a = 0.828}$$

$$y_b = 1 - y_a$$

$$y_b = 1 - 0.827 \ 662 \ 721 \ 9$$

$$y_b = 0.172 \ 337 \ 278 \ 1$$

$$\boxed{y_b = 0.172}$$

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**6.16.** The thermal expansion coefficient  $\alpha = (1/V) (\partial V/\partial T)_p$  is often used when predicting changes in vapor pressure induced by temperature changes. From the relation  $\rho = m/V$ , show that  $\alpha = -(\partial \ln \rho/\partial T)_p$ .

**Solution:**

To solve this problem, we first take the natural logarithm of the density expression to cast it into a more useful form.

$$\rho = \frac{m}{V}$$

$$\ln \rho = \ln \left( \frac{m}{V} \right) = \ln m - \ln V$$

Taking the partial derivative with respect to  $T$  gives,

$$\left( \frac{\partial \ln \rho}{\partial T} \right)_p = \cancel{\frac{\partial \ln m}{\partial T}} - \left( \frac{\partial \ln V}{\partial T} \right)_p$$

$$\left( \frac{\partial \ln \rho}{\partial T} \right)_p = - \left( \frac{\partial \ln V}{\partial T} \right)_p$$

$$\left( \frac{\partial \ln \rho}{\partial T} \right)_p = - \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

The thermal expansion coefficient is given by  $\alpha = (1/V) (\partial V/\partial T)_p$ , hence,

$$\left( \frac{\partial \ln \rho}{\partial T} \right)_p = - \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\alpha$$

$$\boxed{\alpha = - \left( \frac{\partial \ln \rho}{\partial T} \right)_p}$$

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**6.17.** At 293.15 K the density of water is  $0.998\,234\text{ g cm}^{-3}$  and at 294.15 K it is  $0.998\,022\text{ g cm}^{-3}$  under 1 atm of pressure. Estimate the value of  $\alpha$  for water at 1 atm.

**Solution:**

Given:  $T = 293.15\text{ K}$ ,  $\rho_{\text{water}} = 0.998234\text{ g cm}^{-3}$ ,  $T = 294.15\text{ K}$ ,  $\rho_{\text{water}} = 0.998022\text{ g cm}^{-3}$ ,  $P = 1\text{ atm}$

Required:  $\alpha$

To solve this problem, we can use the expression for  $\alpha$  obtained in problem 6.16

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \approx \frac{1}{V} \frac{\Delta V}{\Delta T}$$

We make the approximation since we are considering small changes in  $T$  and  $V$ .

Density is given by,  $\rho = \frac{m}{V}$ , and can be rearranged to solve for  $V$ . Therefore we obtain the expression,

$$\alpha = \frac{1}{V_1} \left( \frac{V_2 - V_1}{T_2 - T_1} \right)$$

$$\alpha = \frac{\rho_1}{m} \left( \frac{\frac{m}{\rho_2} - \frac{m}{\rho_1}}{T_2 - T_1} \right)$$

We can set  $m$ , the mass of water, equal to 1 gram and solve for  $\alpha$



$$\alpha = \frac{0.998234 \frac{\cancel{\text{g}}}{\text{cm}^3}}{1 \frac{\cancel{\text{g}}}{\text{cm}^3}} \left( \frac{\frac{1 \frac{\cancel{\text{g}}}{\text{cm}^3}}{0.998022 \frac{\cancel{\text{g}}}{\text{cm}^3}} - \frac{1 \frac{\cancel{\text{g}}}{\text{cm}^3}}{0.998234 \frac{\cancel{\text{g}}}{\text{cm}^3}}}{294.15 \text{ K} - 293.15 \text{ K}} \right)$$

$$\alpha = 2.124\,201\,67 \times 10^{-4} \text{ K}^{-1}$$

$$\boxed{\alpha = 2.1242 \times 10^{-4} \text{ K}^{-1}}$$

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**6.18.** How many theoretical plates are required to separate the mixture shown in Fig. 6.7?

**Solution:**

There are six full horizontal steps and two fractional steps in Figure 6.7. There are therefore approximately six theoretical plates required to separate the mixture.

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**6.19.** A sealed reaction vessel is completely filled with liquid water at 293.15 K and 1.00 atm. If the temperature is raised exactly 6 K and the walls of the vessel remain rigid, what is the pressure in the container if the average value of  $\alpha = 2.85 \times 10^{-4} \text{ K}^{-1}$  and the compressibility coefficient  $\kappa [= -(1/V)(\partial V/\partial P)_T]$  is  $4.49 \times 10^{-5} \text{ atm}^{-1}$ ?

**Solution:**

Given:  $T = 293.15 \text{ K}$ ,  $P = 1 \text{ atm}$ ,  $\Delta T = 6 \text{ K}$ ,  $\alpha = 2.85 \times 10^{-4} \text{ K}^{-1}$ ,  $\kappa = 4.49 \times 10^{-5} \text{ atm}^{-1}$

Required:  $P$

From chapter 3, Eq. 3.139 defines the expansion coefficient as

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

To solve for  $P$  we rearrange the two expressions for  $\alpha$  and  $\kappa$  in the following manner,

$$\text{From } \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial V}{\partial P} \right)_T = -1$$

$$\frac{\alpha}{\kappa} = \left[ \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \right] \left[ -V \left( \frac{\partial P}{\partial V} \right)_T \right]$$

$$\frac{\alpha}{\kappa} = \left( \frac{\partial P}{\partial T} \right)_V$$

Therefore

$$\Delta P \approx \frac{\alpha}{\kappa} \Delta T = \frac{2.85 \times 10^{-4} \text{ K}^{-1}}{4.49 \times 10^{-5} \text{ atm}^{-1}} \times 6 \text{ K}$$

$$\Delta P = 38.084 \text{ 632 52 atm}$$

$$\boxed{\Delta P = 38.1 \text{ atm}}$$

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**6.20.** In Figure 6.16, a solution having composition  $p$  is cooled to just above the eutectic temperature (point  $s$  is about  $0.18 x_{Si}$ , and  $x_e$  is  $0.31 x_{Si}$ ); calculate the composition of the solid that separates and that of the liquid that remains.

**Solution:**

Given: Figure 6.16,  $x_s = 0.18x_{Si}$ ,  $x_e = 0.31x_{Si}$

Required:  $p$

Using the lever rule, given by Eq. 6.16, we can solve for the ratio,

$$p = \frac{m_{\text{solid layer}}}{m_{\text{solid layer}} + m_{\text{liquid layer}}}$$

$$p = \frac{0.18}{0.31}$$

$$p = 0.5806451613$$

$$\boxed{p = 0.58}$$

This means that there is 58% solid and 42% liquid in the two-phase region. The overall composition of the liquid above the liquid line is  $x_{Si} = 0.31$ .

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**6.21.** The melting points and heats of fusion of gold and silicon are

	Au	Si
$T/\text{K}$	1337	1683
$\Delta_{\text{fus}} H/\text{J mol}^{-1}$	12 677.5	39 622.5

For the data, calculate the solid-liquid equilibrium lines and estimate the eutectic composition graphically. Compare the result with the values given by Figure 6.16.

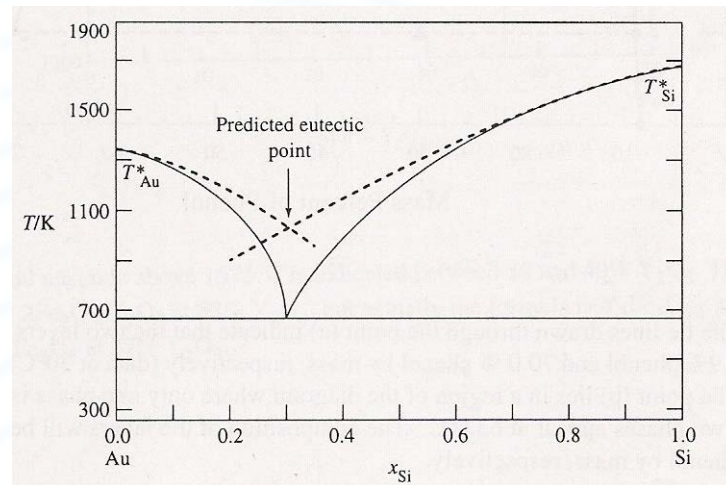
**Solution:**

The temperature at which solid solvent is in equilibrium with liquid solvent, with mole fraction  $x_1$  is given by Eq. 5.115,

$$\ln x_1 = \frac{\Delta_{\text{fus}} H_m}{R} \left( \frac{1}{T_f^*} - \frac{1}{T} \right)$$

Values of  $x_1$  and  $T$  determined from this equation for each component give the desired liquidus lines in the regions near large values of  $x_1$ . Several values are:

$x_1$	$T$ (K)	$x_1$	$T$ (K)
0.945	1650	0.969	1300
0.863	1600	0.924	1250
0.784	1550	0.879	1200
0.708	1500	0.783	1100
0.564	1400	0.681	1000



A plot is shown on which the points represent data points and the solid curves are experimental curves of Figure 6.16. The dotted lines intersect at about  $x_{Si} = 0.28$ , compared to the actual about  $x_{Si} = 0.31$ . However, the eutectic temperature is approximately 400 K too high.

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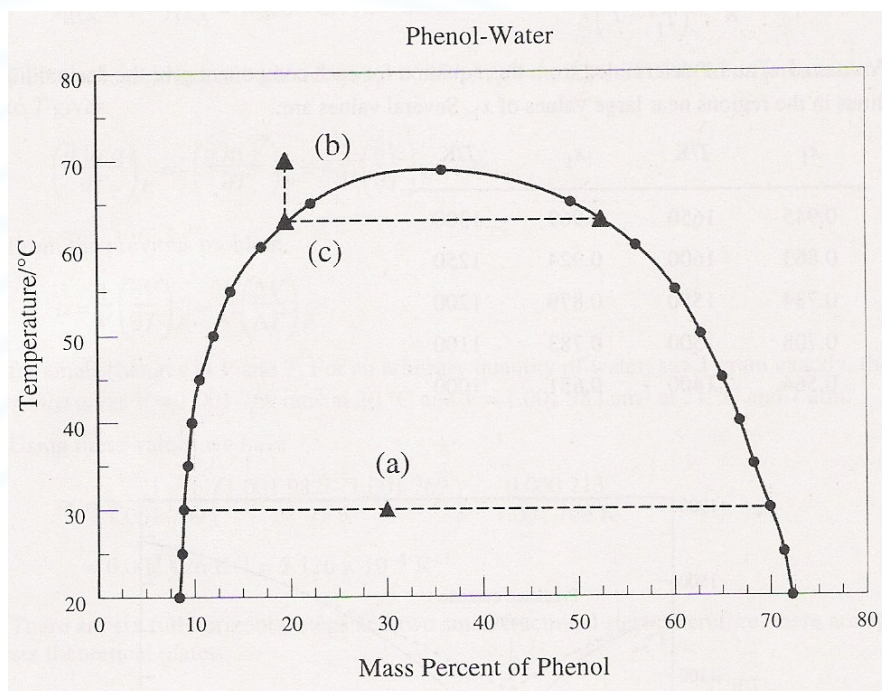
**6.22.** Use the following data to construct a phase diagram of the phenol–water system and answer the following questions (the compositions are given in grams of phenol in 100 grams of solution):

$t/^{\circ}\text{C}$	20	25	30	35	40	
Aqueous layer	8.40	8.71	8.92	9.34	9.78	
Phenol layer	72.24	71.38	69.95	68.28	66.81	
	45	50	55	60	65	68.8
	10.62	12.08	13.88	17.10	22.26	35.90
	65.02	62.83	60.18	56.10	49.34	35.90

- What will be the compositions of the layers formed from a solution of 30 g phenol and 70 g water maintained at 30 °C?
- A solution of 20 g phenol and 80 g water is prepared at 70 °C. How many phases will be present?
- At what temperature will two phases appear if the solution in part (b) is cooled gradually? What will be the compositions of the two phases?

**Solution:**

Graphing the data, we generate a phase diagram of the phenol-water system.



- The tie lines drawn through the point (a) indicate that the two layers will have compositions of approximately 8.92% phenol by mass in the aqueous layer, and 69.95% phenol by mass in the phenol layer at 30 °C.
- The point (b) lies in the region of the diagram where only one phase is present.
- Two phases appear at approximately 63.0 °C. The composition of the two layers will be 19.6% phenol by mass in the aqueous layer and 52.5% phenol by mass in the phenol layer.

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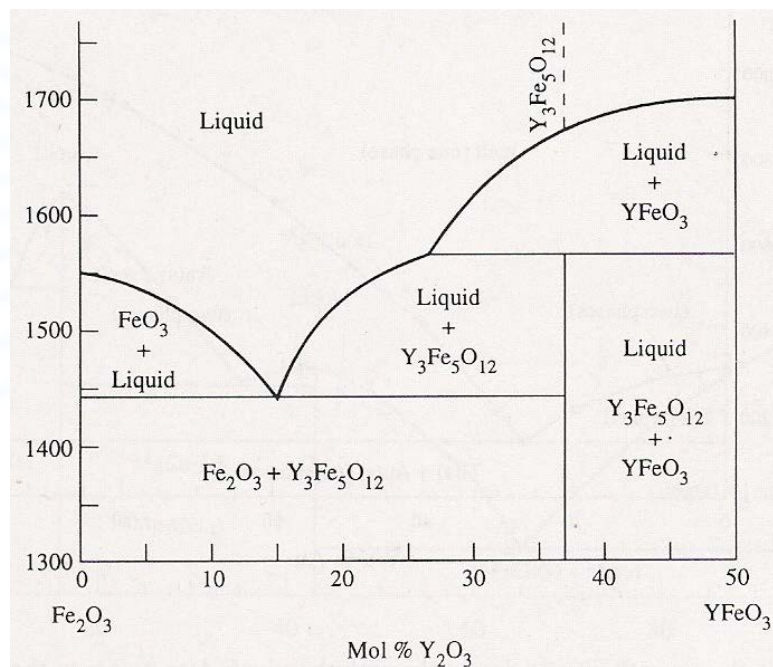
- 6.23.** The following information is obtained from cooling curve data on the partial system  $\text{Fe}_2\text{O}_3\text{--Y}_2\text{O}_3$  [J. W. Nielsen and E. F. Dearborn, *Phys. Chem. Solids*, 5, 203(1958)]:

Composition of Melt/mol % $\text{Y}_2\text{O}_3$	Temperature of Break/ $^\circ\text{C}$	Temperature of Halt/ $^\circ\text{C}$
0		1550
5	1540	1440
10	1515	1440
15	1450	1440
20	1520	1440
25	1560	1440
30	1620	1575/1440
40	1705	1575
50		1720

Sketch the simplest melting point diagram consistent with these data. Label the phase regions and give the composition of any compounds formed.

**Solution:**

Each halt corresponds to a line of three-phase equilibrium and each break to a boundary between a one- and two-phase region. At 50%  $\text{Y}_2\text{O}_3$ , a compound is formed and may be written as  $\text{Fe}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  or  $\text{YFeO}_3$ .



A compound unstable above 1575 °C is indicated between 30% and 40%  $\text{Y}_2\text{O}_3$ . This might be taken to be  $2\text{Fe}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  at 33%  $\text{Y}_2\text{O}_3$ , but actually, the formula is  $\text{Y}_3\text{Fe}_5\text{O}_{12}$ , corresponding to  $3\text{Y}_2\text{O}_3 + 5\text{Fe}_2\text{O}_3$  at 37%  $\text{Y}_2\text{O}_3$ .

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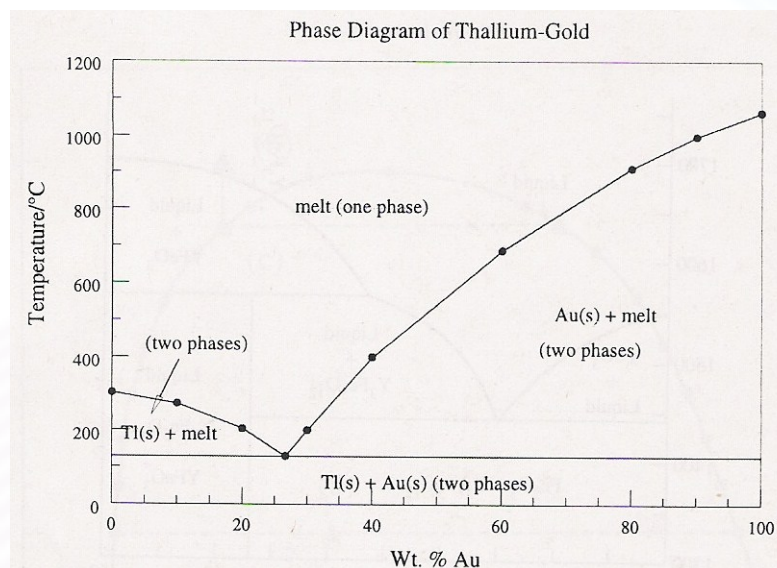
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**6.24.** The study of cooling curves for the thallium–gold system yields the following data. Construct the phase diagram and identify the eutectic composition and temperature. Pure gold melts at 1063 °C and pure thallium melts at 302 °C. In each region, identify the number of phases and the solid that separates out, if any.

Wt % Au	10	20	30	40	60	80	90
First break (°C)	272	204	200	400	686	910	998
Eutectic halt (°C)	128	128	128	128	128	128	128

[Data adapted from A. C. K. Smith, *Applied Physical Chemistry Problems*, London: McGraw-Hill, 1968, p. 13.]

**Solution:**



By extending the smooth curves drawn through the given data points to the eutectic temperature, the composition of the eutectic is identified as 26 wt. % Au.

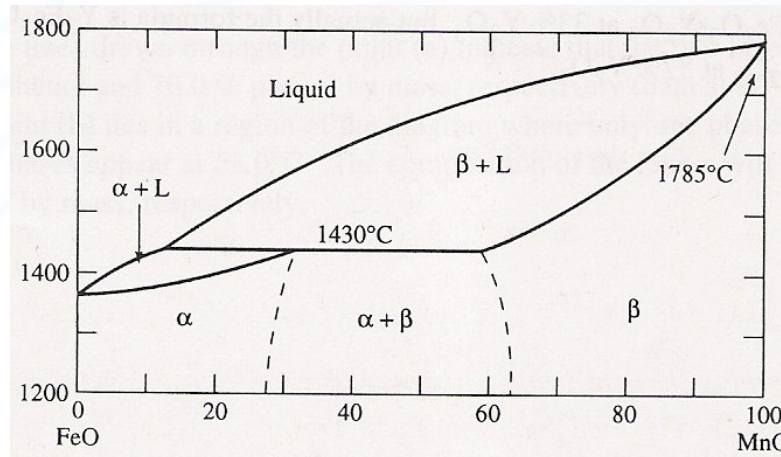
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- 6.25. a.** From the following information, draw the binary phase diagram for the system FeO (mp. 1370 °C)–MnO (mp. 1785 °C). A peritectic reaction occurs at 1430 °C between  $\alpha$  solid solution containing 30 mass % MnO and solid solution containing 60 mass % MnO. These are in equilibrium with melt that contains 15 mass % MnO. At 1200 °C the composition of  $\alpha$  and  $\beta$  solution is 28 mass % and 63 mass %, respectively.
- b.** Describe what happens as a liquid containing 28 mass % MnO is cooled to 1200 °C.

**Solution:**

**a.**



- b.** As liquid of 28 mass % MnO cools,  $\beta$  first forms along with liquid. At 1430 °C,  $\beta$  converts to  $\alpha$  and  $\alpha + L$  remains only briefly at the temperature is lowered about 50 °C, at which point all the liquid is reconverted to the  $\alpha$  phase. The compositions are given by the lever rule. As 1200 °C is approached, some  $\beta$  may again make an appearance.

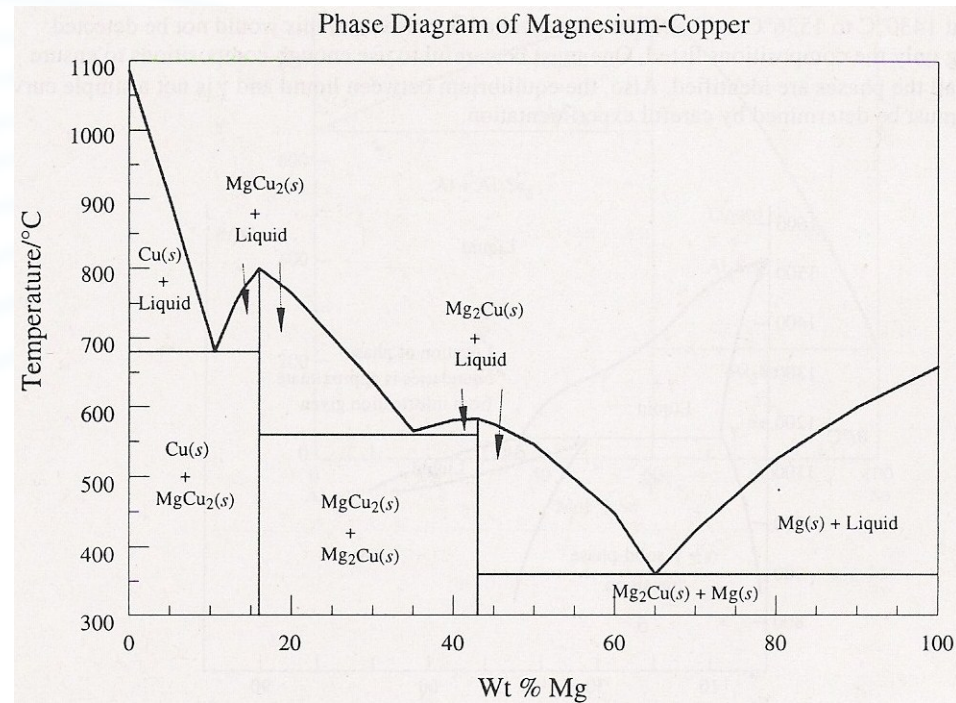
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**6.26.** The following data for the magnesium–copper system is the result of analyzing cooling curves. Pure copper melts at 1085 °C while pure magnesium melts at 659 °C. Two compounds are formed, one at 16.05 wt % Mg with a melting point of 800 °C, and the other at 43.44 wt % Mg with a melting point of 583 °C, respectively. Construct the phase diagram from this information and identify the compositions of the eutectics. [Data adapted from A. C. K. Smith, *Applied Physical Chemistry Problems*, London: McGraw-Hill, 1968, p. 14.]

Wt % Mg	5	10	15	20	30	35		
First break (°C)	900	702	785	765	636	565		
Eutectic halt (°C)	680	680	680	560	560	560		
	40	45	50	60	70	80	90	
	581	575	546	448	423	525	600	
	560	360	360	360	360	360	360	



**Solution:**

From the graph, the first eutectic temperature, 680 °C, has a composition of 10.5 wt. % Mg, the second eutectic temperature, 560 °C, has a composition of 35.0 wt. % Mg, while the third eutectic temperature, 360 °C has a composition of 65 wt. % Mg.

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**6.27.** What are the empirical formulae of the compounds represented by the vertical lines formed in the magnesium–copper system described in Problem 6.26?

**Solution:**

Assuming that there are 100 g of the first compound, we have 16.05 g of Mg and  $100 \text{ g} - 16.05 \text{ g} = 83.95 \text{ g Cu}$ . The mole ratios of Mg : Cu are,

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} = \frac{m_{\text{Mg}} M_{\text{Cu}}}{m_{\text{Cu}} M_{\text{Mg}}}$$

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} = \frac{(16.05 \text{ g})(63.546 \text{ g mol}^{-1})}{(83.95 \text{ g})(24.3050 \text{ g mol}^{-1})}$$

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} = 0.499\,858\,324\,7$$

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} \approx \frac{1}{2}$$

Therefore the empirical formula of the first compound is  $\text{MgCu}_2$ .

Assuming that there are 100 g of the second compound, we have 43.44 g of Mg and  $100 \text{ g} - 43.44 \text{ g} = 56.56 \text{ g Cu}$ . The mole ratios of Mg : Cu are,

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} = \frac{m_{\text{Mg}} M_{\text{Cu}}}{m_{\text{Cu}} M_{\text{Mg}}}$$

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} = \frac{(43.44 \text{ g})(63.546 \text{ g mol}^{-1})}{(56.56 \text{ g})(24.3050 \text{ g mol}^{-1})}$$

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} = 2.008\,043\,001$$

$$\frac{n_{\text{Mg}}}{n_{\text{Cu}}} \approx 2$$

Therefore the empirical formula of the second compound is  $\text{Mg}_2\text{Cu}$ .

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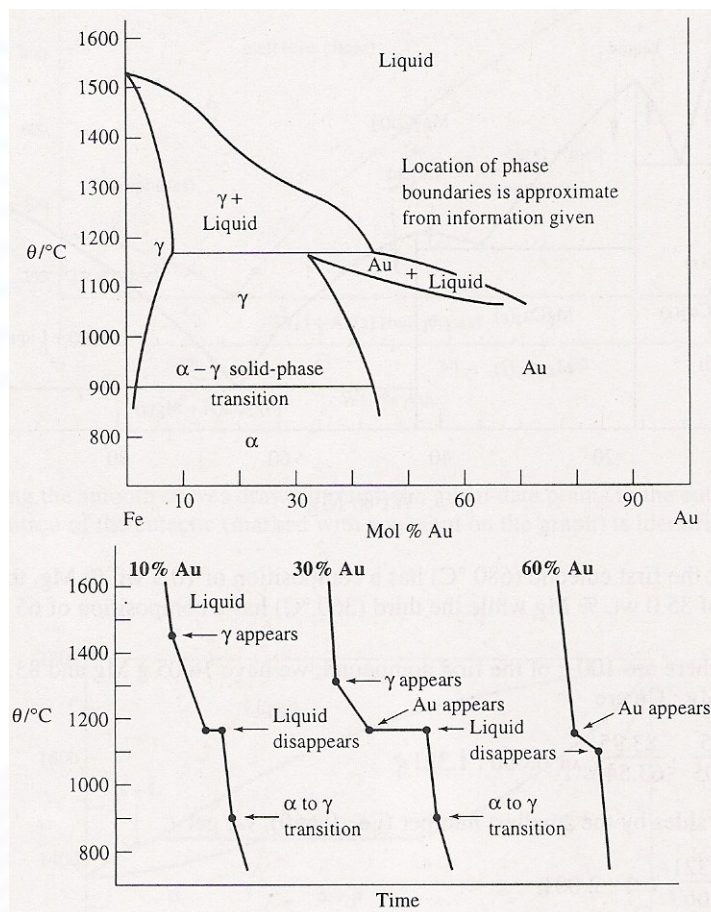
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- 6.28.** A preliminary thermal analysis of the Fe–Au system showed two solid phases of composition 8.1 mol % Au and 25.5 mol % Au in equilibrium at 1168 °C with liquid of composition 43 mol % Au. Construct the simplest melting point diagram consistent with this information and label all the phase regions. Sketch the cooling curves for the composition 10 mol % Au, 30 mol % A, and 60 mol % Au, and make them consistent with the fact that there is an  $\alpha$ - $\gamma$  phase transition in iron at 903 °C and that the  $\gamma$ -phase field extends to 45 mol % Au at this temperature. Iron melts at 1536 °C and gold at 1063 °C.

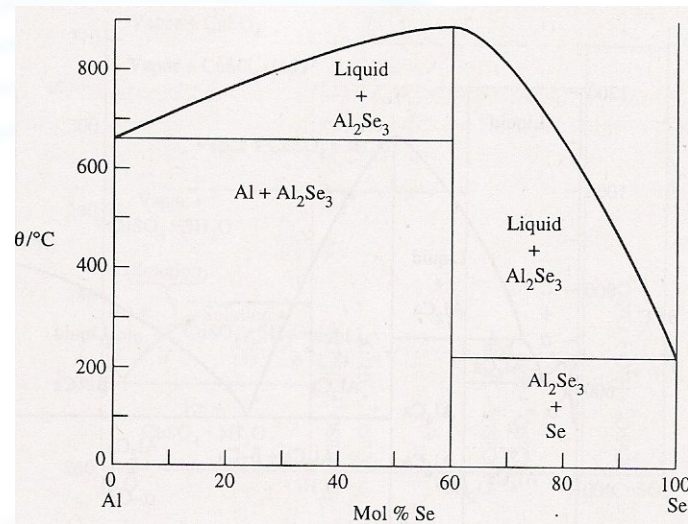
**Solution:**

The coexistence of the three phases is a clear indication of a peritectic-type diagram. A note of caution is in order here: In the range 0–10 mol % Au at 1430 °C to 1536 °C, still another phase, called  $\delta$  exists. This would not be detected using only the compositions listed. One must be careful to use enough composition to ensure that all phases are identified. Also, the equilibrium between liquid and  $\gamma$  is not a simple curve and must be determined by careful experimentation.

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- 6.29.** The aluminum–selenium system was determined from thermal analysis.  $\text{Al}_2\text{Se}_3$  melts congruently at approximately  $950^\circ\text{C}$  and forms a eutectic both with aluminum and with selenium at a very low concentration of the alloying element and at a temperature close to the melting point of the base elements. Draw a diagram from this information and give the composition of the phases. Aluminum melts at  $659.7^\circ\text{C}$  and selenium melts at approximately  $217^\circ\text{C}$ .

**Solution:**



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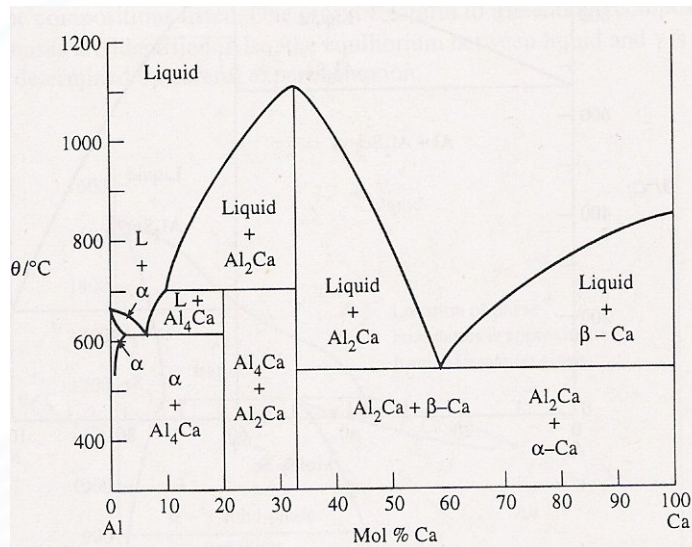
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**\*6.30.** The metals Al and Ca form the compounds  $\text{Al}_4\text{Ca}$  and  $\text{Al}_2\text{Ca}$ . The solids Al, Ca,  $\text{Al}_4\text{Ca}$ , and  $\text{Al}_2\text{Ca}$  essentially are immiscible in each other but are completely miscible as liquids. Maximum Ca solubility in Al is about 2% and occurs at 616 °C. Al melts at 659.7 °C and Ca melts at 848 °C. Compound  $\text{Al}_2\text{Ca}$  melts congruently at 1079 °C and gives a simple eutectic with Ca at 545°C. Compound  $\text{Al}_4\text{Ca}$  decomposes at 700 °C to give  $\text{Al}_2\text{Ca}$  and a melt, the peritectic lying at 10 mol %. A monotectic exists at 616 °C. At approximately 450 °C a transition occurs between  $\alpha$ -Ca and  $\beta$ -Ca.

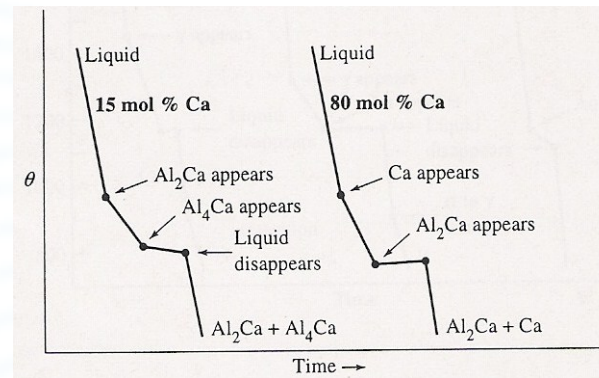
- Draw the simplest phase diagram consistent with this information and label all phase regions.
- Sketch cooling curves for melts of composition 15 mol % Ca and 80 mol % Ca.

**Solution:**

- The lower phase field of the  $\alpha$ -phase is less than 1%

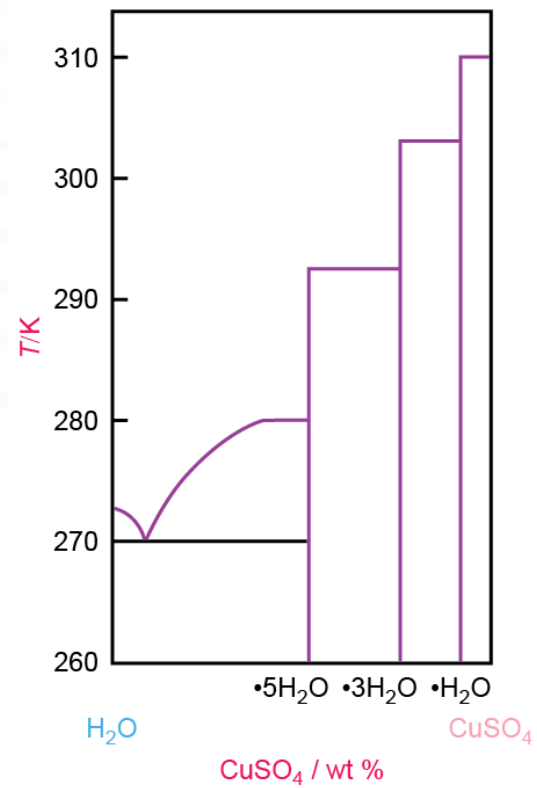


b.

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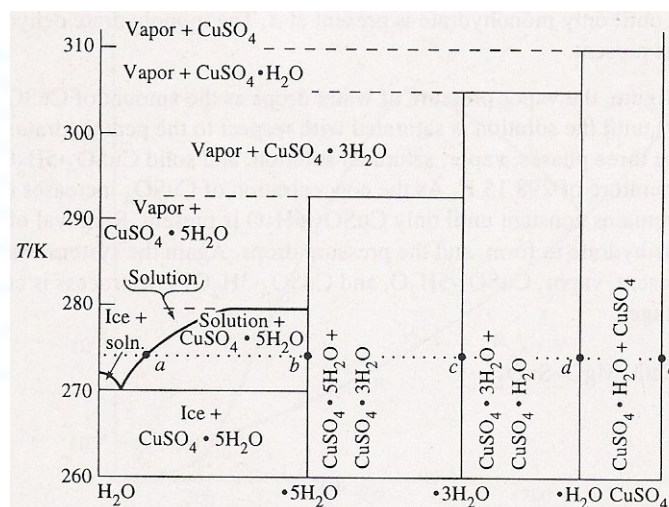
- 6.31.** The extent of dehydration of a salt such as  $\text{CuSO}_4$  can often be followed by measuring the vapor pressure over the hydrated salt. The system  $\text{H}_2\text{O}$ – $\text{CuSO}_4$  is shown in the accompanying figure as an example of such a system. Label the areas as to the phase(s) present. Then describe the sequence of phase changes if a dilute solution of copper sulfate is dehydrated at 275 K, ending with anhydrous copper sulfate. What would a vacuum gauge read starting with pure water during the dehydration process at 298.15 K? Sketch a plot of  $P/\text{Torr}$  against  $\text{CuSO}_4/\text{wt } \%$ . Relevant data are:

The Vapor Pressure of $\text{CuSO}_4$ – $\text{H}_2\text{O}$ at 298.15 K	$P/\text{Torr}$
Vapor + saturated solution + $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	16
Vapor $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$	7.85
Vapor + $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ + $\text{CuSO}_4 \cdot \text{H}_2\text{O}$	4.32
Vapor + $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ + $\text{CuSO}_4$	0.017
Vapor pressure of water	23.8

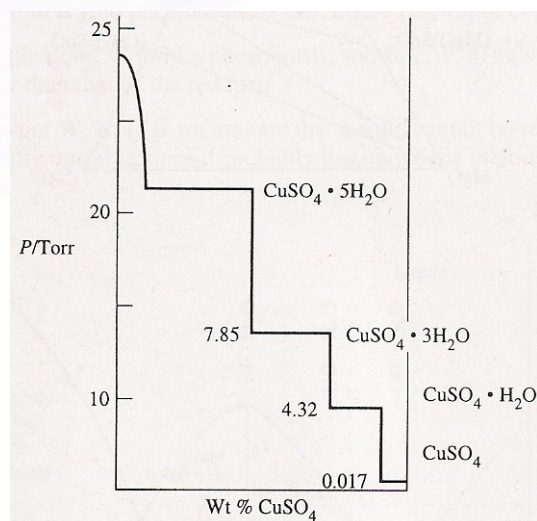


**Solution:**





In the upper figure,  $\text{CuSO}_4$  begins in a solution single-phase region. Pure  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  precipitates out as the first phase boundary at  $a$  is crossed. Water continues to be removed as more  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  precipitates until only pure  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is present at  $b$ . In the next two-phase region,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  dehydrates, forming progressively more  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , until all of the pentahydrate is gone at  $c$ . The process repeats, the trihydrate forming the monohydrate, until only monohydrate is present at  $d$ . The monohydrate dehydrates until at  $e$  only pure  $\text{CuSO}_4$  is present.





In the lower figure, the vapor pressure of water drops as the amount of  $\text{CuSO}_4$  increases, (according to Raoult's Law), until the solution is saturated with respect to the pentahydrate. The system is invariant since three phases, vapor, saturated solution and solid  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , are present at the constant temperature of 298.15 K. As the concentration of  $\text{CuSO}_4$  increases, (water is removed), the pressure remains constant until only  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is present. Removal of additional water causes some trihydrate to form, and the pressure drops. Again the system is invariant; three phases are present, vapor  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ . The process is continued as before at the other stages.

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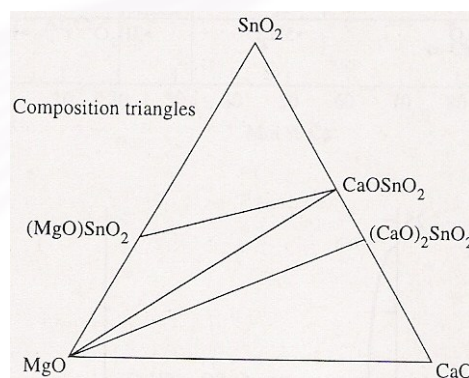
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- 6.32.** The data in the accompanying table are approximate for the isobaric-isothermal system  $\text{SnO}_2$ – $\text{CaO}$ – $\text{MgO}$  at 298.15 K and 1 atm. Sketch a reasonable phase diagram in mol % with  $\text{SnO}_2$  at the apex of the triangle. Label all phase regions; the results are known as composition triangles.

Material	In Equilibrium with Solid Phases
$\text{SnO}_2$	$(\text{MgO})_2\text{SnO}_2$ , $\text{CaOSnO}_2$
$(\text{MgO})_2\text{SnO}_2$	$\text{SnO}_2$ , $(\text{CaO})\text{SnO}_2$ , $\text{MgO}$
$\text{MgO}$	$\text{CaO}$ , $(\text{CaO})_2\text{SnO}_2$
$\text{CaO}$	$\text{MgO}$ , $(\text{CaO})_2\text{SnO}_2$
$(\text{CaO})_2\text{SnO}_2$	$\text{CaO}$ , $\text{MgO}$ , $\text{CaOSnO}_2$
$\text{CaOSnO}_2$	$(\text{CaO})_2\text{SnO}_2$ , $\text{MgO}$ , $(\text{MgO})_2\text{SnO}_2$ , $\text{SnO}_2$

**Solution:**

The system  $\text{SnO}_2$ – $\text{CaO}$ – $\text{MgO}$  is given by,

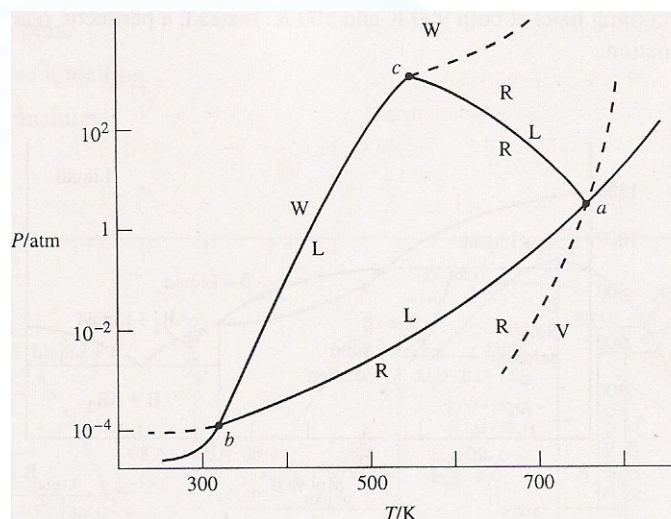


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- 6.33.** Sketch the  $P$  against  $T$  diagram for phosphorous from the following information. White phosphorous melts at 311 K and 0.2 Torr; red phosphorous melts at 763 K and 43 atm. The white form is more dense than the liquid and the red form is less dense than the liquid. The vapor pressure of the white form is everywhere greater than that of the red form. Label each area on the plot, and explain which triple point(s) is (are) stable or metastable.

**Solution:**



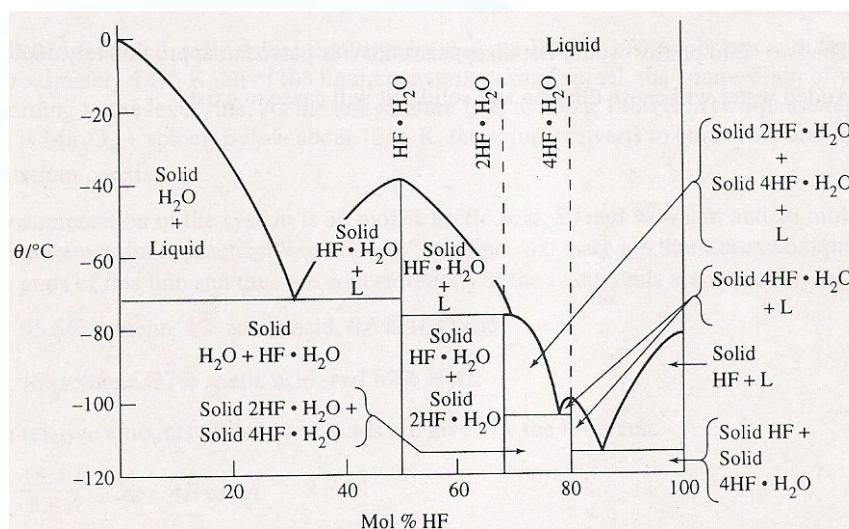
- Stable triple point R (red phosphorus, solid), liquid (L), vapor (V).
- Metastable triple point W (white phosphorus, solid), L, V. The vapor pressure of white phosphorus is greater than that of the red.
- Stable triple point W, R, L. If we assume that a solid cannot be superheated, the triple point W, R, L is totally unstable since it probably lies above the melting point of the liquid.

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- 6.34.** Giguère and Turrell, *J. Am. Chem. Soc.*, 102, 5476(1980), describe three ionic hydrates formed between HF and H<sub>2</sub>O. Sketch the H<sub>2</sub>O-HF phase diagram in mol % HF from the following information. HF · H<sub>2</sub>O melts at −35.2 °C, 2HF · H<sub>2</sub>O decomposes by a peritectic reaction at −75 °C, and 4HF · H<sub>2</sub>O melts at −98.2 °C. HF melts at −83.1 °C. Label the composition of all regions. The eutectic occurs at −111 °C with monotectics at −71 °C, −77 °C, and −102 °C.

**Solution:**



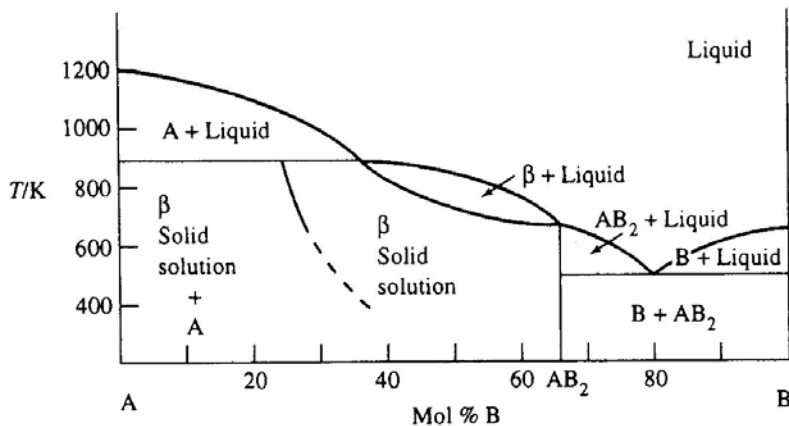
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- 6.35.** In the system A–B a line of three-phase equilibrium occurs at 900 K as determined by thermal analysis. A second three-phase equilibrium occurs at 500 K. Only one halt is observed for any one cooling curve. The compound  $AB_2$  is known and melts at 600 K. If A melts at 1200 K and B at 700 K, sketch the simplest phase diagram consistent with the given data. Label each region.

**Solution:**

The 500 K equilibrium line probably contains a eutectic since the temperature is below the melting points of both  $AB_2$  and B. An unstable compound is ruled out because such a reaction would require cooling halts of both 900 K and 500 K. Instead, a peritectic reaction shown is the simplest explanation.



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**6.36.** The following questions refer to Figure 6.28:

- a. If liquid C were added to the system, what changes would occur if the system originally contained 80% salt A and 20% salt B?
- b. What changes would occur if the system originally contained 50% salt A and 50% salt B upon the addition of liquid?
- c. If liquid is added to an unsaturated solution of salt A and salt B in solution of composition lying at  $e$ , what changes would occur?

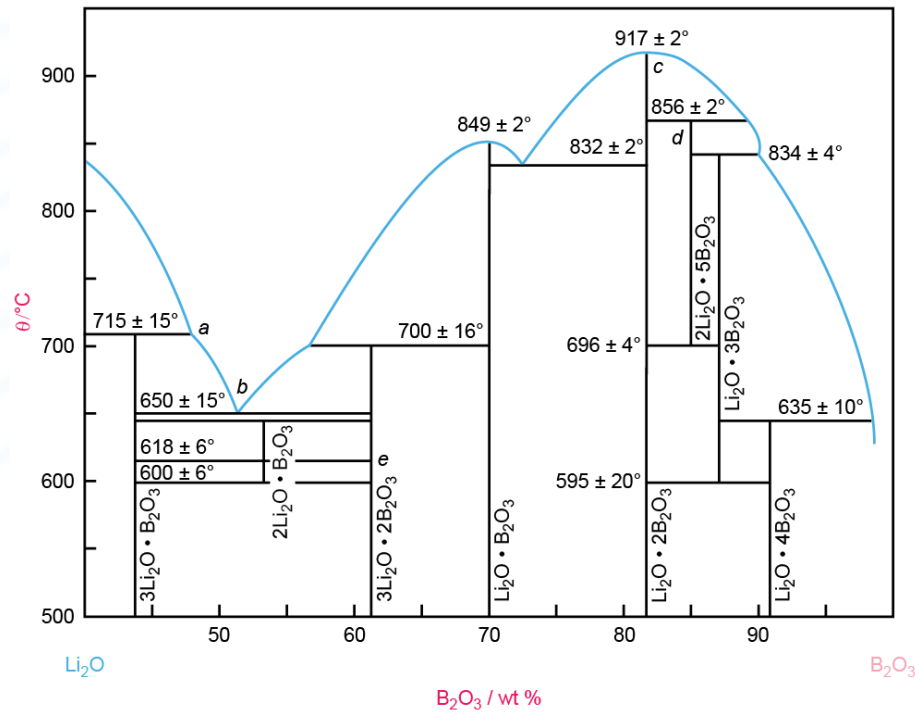
**Solution:**

- a. As liquid C is added, the saturated liquid of composition  $b$  would be in equilibrium with the two solids A and B. At approximately 20% C, when the composition crosses the line  $\overline{bB}$ , the solid A disappears and only solid B will be present in equilibrium with liquid of composition  $b$ .
- b. The two solid phases would not disappear until  $b$  is passed at approximately 50% liquid C.
- c. Added liquid would cause dilution and the solid salt will no longer exist.

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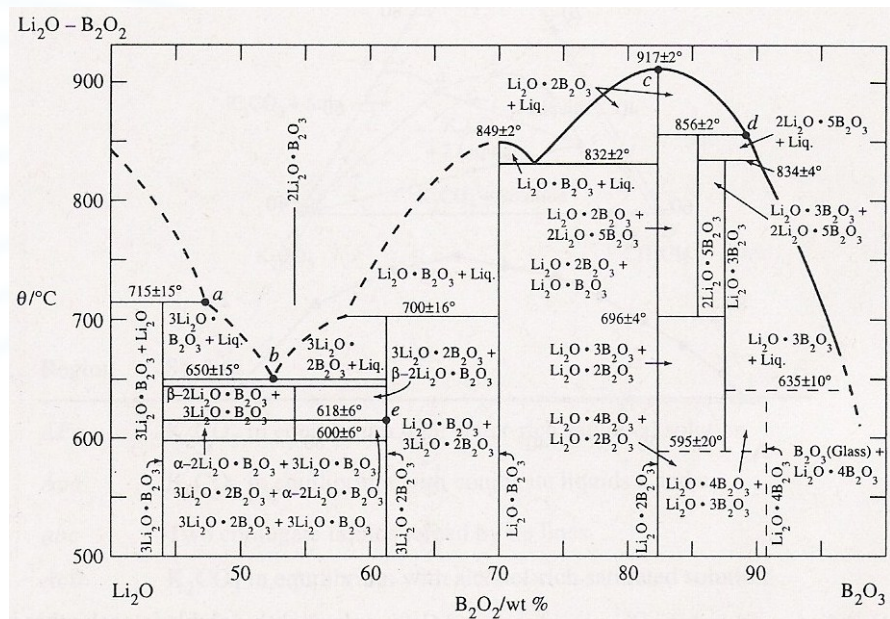
- 6.37.** In the accompanying diagram, due to B. S. R. Sastry and F. A. Hammel, *J. Am. Ceramic Soc.*, 42; 218(1959), identify the composition of all the areas. Identify the phenomenon associated with each lettered position.



[[Diagram for Problem 6.37. Reprinted with permission of The American Ceramic Society, Post Office Box 6136, Westerville, OH 43086-6136, Copyright © 1964 by the American Ceramic Society. All rights reserved.]]



**Solution:**



- a. Peritectic point
- b. Eutectic point
- c. Melting point
- d. Incongruent melting
- e. Phase transition

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**6.38.** Describe what happens within the system  $\text{Mn}_2\text{O}_3\text{--Al}_2\text{O}_3$  in Fig. 6.21 when a liquid of  $x_{\text{Al}_2\text{O}_3} = 0.2$  is cooled from 2100 K to 1200 K.

**Solution:**

At 2100 K, the mixture is in the liquid state. As the liquid is cooled, solid spinel first appears at about 1950 K in equilibrium with liquid. At approximately 1875 K, all of the liquid converts to solid spinel, the composition of which varies according to the lever rule.

As the temperature falls to about 1400 K, a two-phase region appears that is  $\text{Mn}_3\text{O}_4^+$  spinel. Below about 1285 K, the spinel converts to corundum and  $\text{Mn}_3\text{O}_4^+$  corundum coexist.

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- 6.39.** The isobaric solubility diagram for the system acetic acid–toluene–water is shown in Figure 6.27. What phase(s) and their composition(s) will be present if 0.2 mol of toluene is added to a system consisting of 0.5 mol of water and 0.3 mol of acetic acid? Give the relative amounts of each phase.

**Solution:**

Given: Figure 6.27,  $n_{\text{toluene}} = 0.2 \text{ mol}$ ,  $n_{\text{water}} = 0.5 \text{ mol}$ ,  $n_{\text{acetic acid}} = 0.3 \text{ mol}$

Required: phases, composition, relative amounts

Using the number of moles present, the composition of the system is 20% toluene, 50% water and 30% acetic acid.

The system point is practically on the  $\overline{p''q''}$  tie line, and there are therefore two liquids present. The ends of this line, and thus the concentrations of the two liquids are approximately,

- a. 95.5% toluene, 4% acetic acid, 0.5% water
- b. 1% toluene, 37% acetic acid, 62% water

To calculate the relative amounts of the two liquids, we can use the lever rule, given by Eq. 6.16,

$$\frac{n_1}{n_v} = \frac{y_1 - x_T}{x_T - x_1} = \frac{\overline{pv}}{\overline{lp}}$$

$$\frac{15.4 B}{3.8 A} \text{ or } 4B \text{ to } 1A$$

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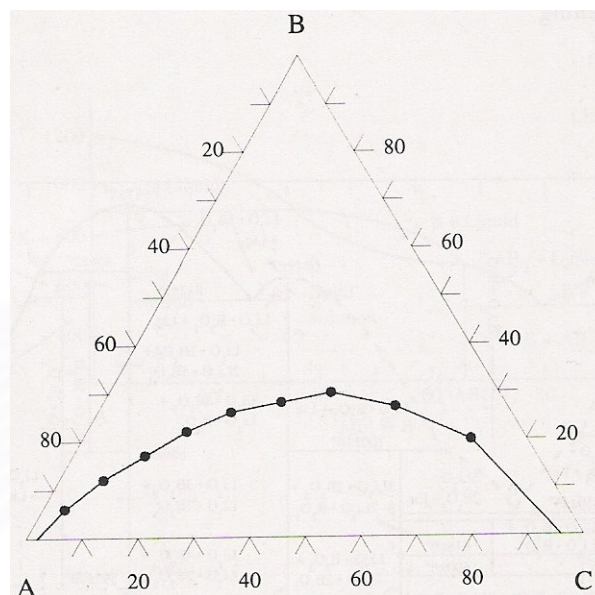
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**6.40.** A fictitious ternary system composed of liquids A, B, and C was constructed by adding the component B to various binary A–C mixtures and noting the point at which complete miscibility occurred. The following are the mole-percents of A and B at which complete miscibility was observed. Construct the phase diagram on a triangular graph paper.

$x_A(\%)$	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0
$x_B(\%)$	20.0	27.0	30.0	28.0	26.0	22.0	17.0	12.0	7.0

Comment on the variation of the mutual solubility of A and C as B is added.

**Solution:**

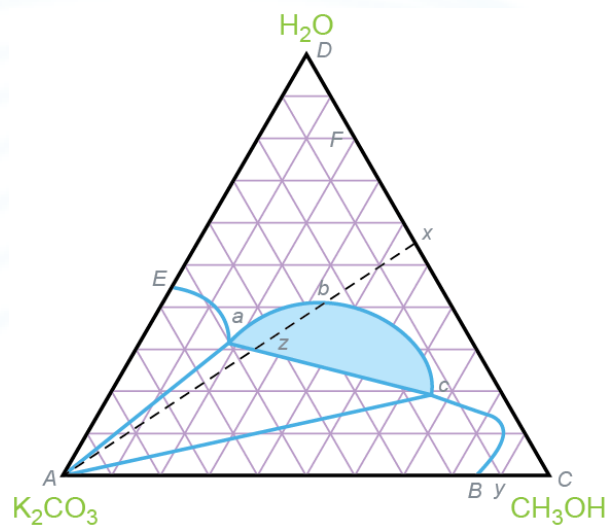


It is clear from the phase diagram that A and C are only slightly soluble in each other in the absence of B. As B is added, two layers are formed; one rich in A, and the other rich in C. As B is added, the mutual solubility of A and C increases until at 30 mole % in B, the three liquids become miscible in all proportions.

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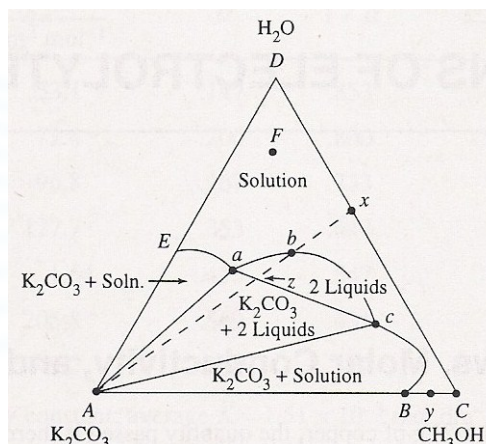
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- 6.41.** In organic chemistry it is a common procedure to separate a mixture of an organic liquid in water by adding a salt to it. This is known as “salting out.” The ternary system  $\text{K}_2\text{CO}_3\text{--H}_2\text{O--CH}_3\text{OH}$  is typical. The system is distinguished by the appearance of the two-liquid region  $abc$ .



- Describe the phase(s) present in each region of the diagram.
- What would occur as solid  $\text{K}_2\text{CO}_3$  is added to a solution of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  of composition  $x$ ?
- How can the organic-rich phase in (b) be separated?
- How can  $\text{K}_2\text{CO}_3$  be precipitated from a solution having composition  $y$ ?
- Describe in detail the sequence of events when a solution of composition  $F$  is evaporated.

**Solution:**



**a.**

Region	System
<i>AEa</i>	K <sub>2</sub> CO <sub>3</sub> in equilibrium with water-rich saturated solution
<i>Aac</i>	K <sub>2</sub> CO <sub>3</sub> in equilibrium with conjugate liquids a and c
<i>abc</i>	Two conjugate liquids joined by tie lines
<i>AcB</i>	K <sub>2</sub> CO <sub>3</sub> in equilibrium with alcohol-rich saturated solution

- b. The state of the system will move along a line joining  $x$  and  $A$ . Initially solution is formed; as more  $K_2CO_3$  is added, two layers,  $a$  and  $c$  form, and once beyond point  $z$ ,  $K_2CO_3$  ceases to dissolve so that solid  $K_2CO_3$  and the two liquids  $a$  and  $c$  coexist.
- c. As long as two liquids exist, liquid with composition in the region  $AcB$  is the alcohol-rich layer and may be separated from the water-rich later by separatory funnel.
- d. When water is added to an unsaturated solution of  $K_2CO_3$  in alcohol, the state of the system moves along the line joining  $y$  and  $D$ . Some  $K_2CO_3$  will precipitate as the state moves into the  $ABc$  region and then redissolves as it moves into the solution region again.
- e. On evaporation of  $F$ , the system composition follows a line drawn from the water corner through  $F$  to the  $Ac$  line. At the first composition line, two liquids form and the compositions of the solutions of the solutions move toward  $a$  and  $c$ . When the system composition reaches the  $ac$  line,  $K_2CO_3$  begins to precipitate and is in equilibrium with the conjugate liquids  $a$  and  $c$ . Further reduction of water moves the ratio of liquid  $a$  to liquid  $c$  in favor of  $c$  until the line  $Ac$  is crossed, at which time solid  $K_2CO_3$  is in equilibrium with a single solution.

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CHAPTER 7

Solutions of Electrolytes

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Physical Chemistry

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Problems and Solutions

## Chapter 7

*\*problems with an asterisk are slightly more demanding*

## Faraday's Laws, Molar Conductivity, and Weak Electrolytes

- 7.1.** A constant current was passed through a solution of cupric sulfate,  $\text{CuSO}_4$ , for 1 h, and 0.040 g of copper was deposited. Calculate the current (atomic weight of Cu = 63.5).

[Solution](#)

- 7.2.** After passage of a constant current for 45 min, 7.19 mg of silver (atomic weight = 107.9) was deposited from a solution of silver nitrate. Calculate the current.

[Solution](#)

- 7.3.** Electrolysis of molten KBr generates bromine gas, which can be used in industrial bromination processes. How long will it take to convert a 500.00-kg batch of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) to monobromophenol using a current of 20 000 A?

[Solution](#)

- 7.4.** The following are the molar conductivities  $\Lambda$  of chloroacetic acid in aqueous solution at 25 °C and at various concentrations  $c$ :

$\frac{c}{10^{-4} M}$	625	312.5	156.3	78.1	39.1	19.6	9.8
$\frac{\Lambda}{\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$	53.1	72.4	96.8	127.7	164.0	205.8	249.2

Plot  $\Lambda$  against  $c$ . If  $\Lambda^\circ = 362 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , are these values in accord with the Ostwald dilution law? What is the value of the dissociation constant? (See also Problem 7.11.)

[Solution](#)

- 7.5.** The electrolytic conductivity of a saturated solution of silver chloride,  $\text{AgCl}$ , in pure water at 25 °C is  $1.26 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  higher than that for the water used. Calculate the solubility of  $\text{AgCl}$  in water if the molar ionic conductivities are  $\text{Ag}^+$ ,  $61.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ;  $\text{Cl}^-$ ,  $76.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

[Solution](#)



- \*7.6.** The electrolytic conductivity of a 0.001 *M* solution of  $\text{Na}_2\text{SO}_4$  is  $2.6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ . If the solution is saturated with  $\text{CaSO}_4$ , the conductivity becomes  $7.0 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ . Calculate the solubility product for  $\text{CaSO}_4$  using the following molar conductivities at these concentrations:  $\lambda(\text{Na}^+) = 50.1 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ;  $\lambda\left(\frac{1}{2}\text{Ca}^{2+}\right) = 59.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

[Solution](#)

- 7.7.** The quantity  $l/A$  of a conductance cell (see Eq. 7.8) is called the cell constant. Find the cell constant for a conductance cell in which the conductance,  $G$ , of a 0.100 *M* KCl solution is 0.01178 S at 25 °C. The equivalent conductance for 0.100 *M* KCl at 25 °C is  $128.96 \text{ S cm}^2 \text{mol}^{-1}$ . If a 0.0500 *M* solution of an electrolyte has a measured conductance of 0.00824 S using this cell, what is the equivalent conductance of the electrolyte?

[Solution](#)

- \*7.8.** A conductivity cell when standardized with 0.01 *M* KCl was found to have a resistance of 189  $\Omega$ . With 0.01 *M* ammonia solution the resistance was 2460  $\Omega$ . Calculate the base dissociation constant of ammonia, given the following molar conductivities at these concentrations:  $\lambda(\text{K}^+) = 73.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ;  $\lambda(\text{Cl}^-) = 76.4 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ;  $\lambda(\text{NH}_4^+) = 73.4 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ;  $\lambda(\text{OH}^-) = 198.6 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

[Solution](#)

- 7.9.** The conductivity of a 0.0312 *M* solution of a weak base is  $1.53 \times 10^{-4} \text{ S cm}^{-1}$ . If the sum of the limiting ionic conductances for  $\text{BH}^+$  and  $\text{OH}^-$  is  $237.0 \text{ S cm}^2 \text{mol}^{-1}$ , what is the value of the base constant  $K_b$ ?

[Solution](#)

- 7.10.** The equivalent conductance of KBr solutions as a function of concentration at 25 °C is given in the following table. By a linear regression analysis of suitable variables, find the value of  $\Lambda^\circ$  for KBr.

$c/10^{-3} \text{ M}$	0.25	0.36	0.50	0.75	1.00	1.60	2.00	5.00	10.00
$\Lambda/\text{S cm}^2 \text{mol}^{-1}$	150.16	149.87	149.55	149.12	148.78	148.02	147.64	145.47	143.15

[Solution](#)



- 7.11.** Equation 7.20 is one form of Ostwald's dilution law. Show how it can be linearized (i.e., convert it into a form that will allow experimental values of  $\Lambda$  at various concentrations to be tested by means of a straight-line plot). Explain how  $\Lambda^\circ$  and  $K$  can be obtained from the plot.

Kraus and Callis, *J. Amer. Chem. Soc.*, 45, 2624(1923), obtained the following electrolytic conductivities  $\kappa$  for the dissociation of tetramethyl tin chloride,  $(\text{CH}_3)_4\text{SnCl}$ , in ethyl alcohol solution at 25.0 °C and at various concentrations  $c$ :

$c/10^{-4} \text{ mol dm}^{-3}$	1.566	2.600	6.219	10.441
$\kappa/10^{-6} \Omega^{-1} \text{ cm}^{-1}$	1.788	2.418	4.009	5.336

By the use of the linear plot you have devised, determine  $\Lambda^\circ$  and  $K$ .

[Solution](#)

- 7.12.** A certain chemical company wishes to dispose of its acetic acid waste into a local river by first diluting it with water to meet the regulation that the total acetic acid concentration cannot exceed 1500 ppm by weight. You are asked to design a system using conductance to continuously monitor the acid concentration in the water and trigger an alarm if the 1500 ppm limit is exceeded. What is the maximum conductance at which the system should trigger an alarm at a constant temperature of 25 °C? (Assume that the cell constant is  $1.0 \text{ cm}^{-1}$  and that the density of 1500 ppm acetic acid solution is not appreciably different from that of pure water. The  $\Lambda^\circ$  for acetic acid is  $390.7 \text{ S cm}^2 \text{ mol}^{-1}$  and  $K_a = 1.81 \times 10^{-5} \text{ mol dm}^{-3}$  at 25 °C. Ignore the conductance of water.)

[Solution](#)

- 7.13.** How far can the conductivity of water at 25 °C be lowered *in theory* by removing impurities? The  $\Lambda^\circ$  (in  $\text{S cm}^2 \text{ mol}^{-1}$ ) for KOH, HCl, and KCl are, respectively, 274.4, 426.04, and 149.86.  $K_w = 1.008 \times 10^{-14}$ . Compare your answer to the *experimental* value of  $5.8 \times 10^{-8} \text{ S cm}^{-1}$  obtained by Kohlrausch and Heydweiller, *Z. phys. Chem.* 14, 317(1894).

[Solution](#)

### Debye-Hückel Theory and Transport of Electrolytes

- 7.14.** The radius of the ionic atmosphere ( $1/\kappa$ ) for a univalent electrolyte is 0.964 nm at a concentration of 0.10 M in water at 25 °C ( $\epsilon = 78$ ). Estimate the radius (a) in water at a concentration of 0.0001 M and (b) in a solvent of  $\epsilon = 38$  at a concentration of 0.10 M.

[Solution](#)

- 7.15.** The molar conductivities of 0.001 *M* solutions of potassium chloride, sodium chloride, and potassium sulfate  $\left(\frac{1}{2}\text{K}_2\text{SO}_4\right)$  are 149.9, 126.5, and 153.3  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , respectively. Calculate an approximate value for the molar conductivity of a solution of sodium sulfate of the same concentration.

[Solution](#)

- 7.16.** The molar conductivity at 18 °C of a 0.0100 *M* aqueous solution of ammonia is 9.6  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . For  $\text{NH}_4\text{Cl}$ ,  $\Lambda^\circ = 129.8\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$  and the molar ionic conductivities of  $\text{OH}^-$  and  $\text{Cl}^-$  are 174.0 and 65.6  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , respectively. Calculate  $\Lambda^\circ$  for  $\text{NH}_3$  and the degree of ionization in 0.01 *M* solution.

[Solution](#)

- 7.17.** A solution of  $\text{LiCl}$  was electrolyzed in a Hittorf cell. After a current of 0.79 A had been passed for 2 h, the mass of  $\text{LiCl}$  in the anode compartment had decreased by 0.793 g.

a. Calculate the transport numbers of the  $\text{Li}^+$  and  $\text{Cl}^-$  ions.

b. If  $\Lambda^\circ(\text{LiCl})$  is 115.0  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , what are the molar ionic conductivities and the ionic mobilities?

[Solution](#)

- 7.18.** A solution of cadmium iodide,  $\text{CdI}_2$ , having a molality of  $7.545 \times 10^{-3}\text{mol kg}^{-1}$ , was electrolyzed in a Hittorf cell. The mass of cadmium deposited at the cathode was 0.03462 g. Solution weighing 152.64 g was withdrawn from the anode compartment and was found to contain 0.3718 g of cadmium iodide. Calculate the transport numbers of  $\text{Cd}^{2+}$  and  $\text{I}^-$ .

[Solution](#)

- 7.19.** The transport numbers for  $\text{HCl}$  at infinite dilution are estimated to be  $t^+ = 0.821$  and  $t^- = 0.179$  and the molar conductivity is 426.16  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . Calculate the mobilities of the hydrogen and chloride ions.

[Solution](#)

- 7.20.** If a potential gradient of 100  $\text{V cm}^{-1}$  is applied to a 0.01 *M* solution of  $\text{NaCl}$ , what are the speeds of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions? Take the ionic conductivities to be those listed in Table 7.3 on p. 291.

[Solution](#)

- \*7.21.** A solution of LiCl at a concentration of 0.01  $M$  is contained in a tube having a cross-sectional area of 5 cm<sup>2</sup>. Calculate the speeds of the Li<sup>+</sup> and Cl<sup>-</sup> ions if a current of 1 A is passed. Use the ion conductivities listed in Table 7.3.

[Solution](#)

- 7.22.** What is the work required to separate in vacuum two particles, one with the charge of the proton, from another particle with the same charge of opposite sign? Carry out the calculations for an initial distance of (a) 1.0 nm to an infinite distance apart and (b) from 1.0 mm to an infinite distance apart. (c) In (a) how much work would be required if the charge is moved to a distance of 0.1 m? The charge on a proton is  $1.6 \times 10^{-19}$  C.

[Solution](#)

- \*7.23.** According to Bjerrum's theory of ion association, the number of ions of type  $i$  present in a spherical shell of thickness  $dr$  and distance  $r$  from a central ion is

$$dN_i = N_i \exp(-z_i z_c e^2 / 4\pi \epsilon_0 \epsilon r k_B T) 4\pi r^2 dr$$

where  $z_i$  and  $z_c$  are the charge numbers of the ion of type  $i$  and of the central ion and  $e$ ,  $\epsilon_0$ ,  $\epsilon$ , and  $k_B$  have their usual significance. Plot the exponential in this expression and also  $4\pi r^2$  against  $r$  for a uni-univalent electrolyte in water at 25.0 °C ( $\epsilon = 78.3$ ). Allow  $r$  to have values from 0 to 1 nm. Plot also the product of these functions, which is  $(dN_i/N_i)dr$  and is the probability of finding an ion of type  $i$  at a distance between  $r$  and  $r + dr$  of the central ion.

By differentiation, obtain a value  $r^*$  for which the probability is a minimum, and calculate the value for water at 25.0 °C. The electrostatic potential is given to a good approximation by the first term in Eq. 7.47 on p. 280. Obtain an expression, in terms of  $k_B T$ , for the electrostatic energy between the two univalent ions at this minimum distance, and evaluate this energy at 25 °C.

[Solution](#)

**Thermodynamics of Ions**

**7.24.** The following are some conventional standard enthalpies of ions in aqueous solution at 25 °C:

Ion	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{H}^+$	0
$\text{Na}^+$	-239.7
$\text{Ca}^{2+}$	-543.1
$\text{Zn}^{2+}$	-152.3
$\text{Cl}^-$	-167.4
$\text{Br}^-$	-120.9

Calculate the enthalpy of formation in aqueous solution of 1 mol of NaCl, CaCl<sub>2</sub>, and ZnBr<sub>2</sub>, assuming complete dissociation.

[Solution](#)

**7.25.** One estimate for the absolute Gibbs energy of hydration of the  $\text{H}^+$  ion in aqueous solution is  $-1051.4 \text{ kJ mol}^{-1}$ . On this basis, calculate the absolute Gibbs energies of hydration of the following ions, whose conventional standard Gibbs energies of hydration are as follows:

Ion	$\Delta_{\text{hyd}} G^\circ / \text{kJ mol}^{-1}$
$\text{H}^+$	0
$\text{Na}^+$	679.1
$\text{Mg}^{2+}$	274.1
$\text{Al}^{3+}$	-1346.4
$\text{Cl}^-$	-1407.1
$\text{Br}^-$	-1393.3

[Solution](#)

- 7.26.** Calculate the ionic strengths of 0.1 *M* solutions of KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, ZnSO<sub>4</sub>, ZnCl<sub>2</sub>, and K<sub>4</sub>Fe(CN)<sub>6</sub>; assume complete dissociation and neglect hydrolysis.

[Solution](#)

- 7.27.** Calculate the mean activity coefficient  $\gamma_{\pm}$  for the Ba<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions in a saturated solution of BaSO<sub>4</sub> ( $K_{\text{sp}} = 9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ ) in 0.2 *M* K<sub>2</sub>SO<sub>4</sub>, assuming the Debye-Hückel limiting law to apply.

[Solution](#)

- 7.28.** The solubility of AgCl in water at 25 °C is  $1.274 \times 10^{-5} \text{ mol dm}^{-3}$ . On the assumption that the Debye-Hückel limiting law applies,

- Calculate  $\Delta G^\circ$  for the process  $\text{AgCl(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ .
- Calculate the solubility of AgCl in an 0.005 *M* solution of K<sub>2</sub>SO<sub>4</sub>.

[Solution](#)

- 7.29.** Employ Eq. 7.114 to make plots of  $\log \gamma_{\pm}$  against  $\sqrt{I}$  for a uni-univalent electrolyte in water at 25 °C, with  $B = 0.51 \text{ mol}^{-1} \text{ dm}^{3/2}$  and  $B' = 0.33 \times 10^{10} \text{ mol}^{-1} \text{ dm}^{3/2} \text{ m}^{-1}$ , and for the following values of the interionic distance  $a$ :

$$a = 0, 0.1, 0.2, 0.4, \text{ and } 0.8 \text{ nm}$$

[Solution](#)

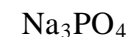
- 7.30.** Estimate the change in Gibbs energy  $\Delta G$  when 1 mol of K<sup>+</sup> ions (radius 0.133 nm) is transported from aqueous solution ( $\epsilon = 78$ ) to the lipid environment of a cell membrane ( $\epsilon = 4$ ) at 25 °C.

[Solution](#)

- 7.31.** At 18 °C the electrolytic conductivity of a saturated solution of CaF<sub>2</sub> is  $3.86 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ , and that of pure water is  $1.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ . The molar ionic conductivities of  $\frac{1}{2}\text{Ca}^{2+}$  and F<sup>-</sup> are  $51.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and  $47.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively. Calculate the solubility of CaF<sub>2</sub> in pure water at 18 °C and the solubility product.

[Solution](#)

**7.32.** What concentrations of the following have the same ionic strength as 0.1 M NaCl?



Assume complete dissociation and neglect hydrolysis.

[Solution](#)

**7.33.** The solubility product of  $\text{PbF}_2$  at 25.0 °C is  $4.0 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ . Assuming the Debye-Hückel limiting law to apply, calculate the solubility of  $\text{PbF}_2$  in (a) pure water and (b) 0.01 M NaF.

[Solution](#)

**7.34.** Calculate the solubility of silver acetate in water at 25 °C, assuming the DHLL to apply; the solubility product is  $4.0 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}$ .

[Solution](#)

**\*7.35.** Problem 7.30 was concerned with the Gibbs energy change when 1 mol of  $\text{K}^+$  ions are transported from water to a lipid. Estimate the electrostatic contribution to the entropy change when this occurs, assuming the dielectric constant of the lipid to be temperature independent, and the following values for water at 25 °C:  $\epsilon = 78$ ;  $\partial \ln \epsilon / \partial T = -0.0046 \text{ K}^{-1}$ . Suggest a qualitative explanation for the sign of the value you obtain.

[Solution](#)

**\*7.36.** Assuming the Born equation (Eq. 7.86) to apply, make an estimate of the reversible work of charging 1 mol of  $\text{Na}^+\text{Cl}^-$  in aqueous solution at 25 °C ( $\epsilon = 78$ ), under the following conditions:

a. The electrolyte is present at infinite dilution.

b. The electrolyte is present at such a concentration that the mean activity coefficient is 0.70.

The ionic radii are 95 pm for  $\text{Na}^+$  and 181 pm for  $\text{Cl}^-$ .

[Solution](#)

**7.37.** If the solubility product of barium sulfate is  $9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ , calculate the solubility of  $\text{BaSO}_4$  in a solution that is 0.10 M in  $\text{NaNO}_3$  and 0.20 M in  $\text{Zn}(\text{NO}_3)_2$ ; assume the DHLL to apply.

[Solution](#)



- 7.38.** Silver chloride, AgCl, is found to have a solubility of  $1.561 \times 10^{-5} M$  in a solution that is  $0.01 M$  in  $K_2SO_4$ . Assume the DHLL to apply and calculate the solubility in pure water.

[Solution](#)

- 7.39.** The enthalpy of neutralization of a strong acid by a strong base, corresponding to the process



is  $-55.90 \text{ kJ mol}^{-1}$ . The enthalpy of neutralization of HCN by NaOH is  $-12.13 \text{ kJ mol}^{-1}$ . Make an estimate of the enthalpy of dissociation of HCN.

[Solution](#)

- 7.40.** Make use of the Debye-Hückel limiting law to estimate the activity coefficients of the ions in an aqueous  $0.004 M$  solution of sodium sulfate at 298 K. Estimate also the mean activity coefficient.

[Solution](#)

### Ionic Equilibria

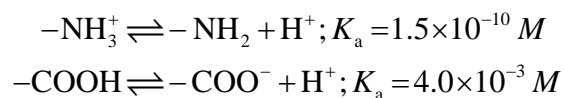
- 7.41.** A  $0.1 M$  solution of sodium palmitate,  $C_{15}H_{31}COONa$ , is separated from a  $0.2 M$  solution of sodium chloride by a membrane that is permeable to  $Na^+$  and  $Cl^-$  ions but not to palmitate ions. Calculate the concentrations of  $Na^+$  and  $Cl^-$  ions on the two sides of the membrane after equilibrium has become established. (For a calculation of the Nernst potential, see Problem 8.18.)

[Solution](#)

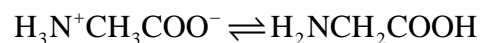
- 7.42.** Consider the ionizations



Assume that the following acid dissociation constants apply to the ionizations:



Estimate a value for the equilibrium constant for the process



[Solution](#)

**7.43.** The  $pK$  values for the successive ionizations of phosphoric acid are given on p. 308. Which of the four species is predominant at the following values of the hydrogen or hydroxide concentration?

- a.  $[H^+] = 0.1\ M$ .
- b.  $[H^+] = 2 \times 10^{-3}\ M$ .
- c.  $[H^+] = 5 \times 10^{-5}\ M$ .
- d.  $[OH^-] = 2 \times 10^{-3}\ M$ .
- e.  $[OH^-] = 1\ M$ .

[Solution](#)

**7.44.** Two solutions of equal volume are separated by a membrane which is permeable to  $K^+$  and  $Cl^-$  ions but not to  $P^-$  ions. The initial concentrations are as shown below.

$$[K^+] = 0.05\ M$$

$$[Cl^-] = 0.05\ M$$

$$[K^+] = 0.15\ M$$

$$[P^-] = 0.15\ M$$

Calculate the concentrations on each side of the membrane after equilibrium has become established. (See Problem 8.26 in Chapter 8 for the calculation of the Nernst potential for this system.)

[Solution](#)

### Essay Questions

- 7.45.** State Faraday's two laws of electrolysis and discuss their significance in connection with the electrical nature of matter.
- 7.46.** Discuss the main ideas that lie behind the Debye-Hückel theory, as applied to the conductivities of solutions of strong electrolytes.
- 7.47.** Outline two important methods for determining transport numbers of ions.
- 7.48.** Explain why  $Li^+$  has a lower ionic conductivity than  $Na^+$  and why the value for  $H^+$  is so much higher than the values for both of these ions.
- 7.49.** Describe briefly the type of hydration found with the following ions in aqueous solution:  $Li^+$ ,  $Br^-$ ,  $H^+$ ,  $OH^-$ .
- 7.50.** What modifications to the Debye-Hückel limiting law are required to explain the influence of ionic strength on solubilities?



**Solutions**

**7.1.** A constant current was passed through a solution of cupric sulfate,  $\text{CuSO}_4$ , for 1 h, and 0.040 g of copper was deposited. Calculate the current (atomic weight of Cu =  $63.5 \text{ g mol}^{-1}$ ).

**Solution:**

Given:  $t = 1 \text{ h} = 3600 \text{ s}$ ,  $m = 0.040 \text{ g}$ ,  $M = 63.5 \text{ g mol}^{-1}$

Required:  $I$

To solve this problem we must use Eq. 7.6 and apply Faraday's Laws of Electrolysis. Eq. 7.6 is given by,

$$Q = It$$

Rearranging to solve for  $I$  we obtain,

$$I = \frac{Q}{t}$$

where  $Q$ , is the quantity of electricity.

$Q$  is proportional to the mass of the element produced at the electrode. Faraday's constant, given by the symbol  $F$ , relates the amount of substance deposited to the quantity of electricity,  $Q$ , passed through the solution. The charge carried by 1 mol of ions bearing  $z$  unit charges is  $zF$ , where  $1 F = 96\,485 \text{ C mol}^{-1}$ .

Hence,

$$Q = zF \left( \frac{m}{M} \right)$$

Using the expression above, we can solve for the current through the solution.

$$I = \frac{zF}{t} \left( \frac{m}{M} \right)$$

The charge on copper in  $\text{CuSO}_4$  is  $\text{Cu}^{2+}$ , therefore  $z = 2$

$$I = \frac{2 \times 96\,485 \text{ C mol}^{-1}}{3600 \text{ s}} \left( \frac{0.040 \text{ g}}{63.5 \text{ g mol}^{-1}} \right)$$

$$I = 0.033\,765\,529\,3 \text{ C s}^{-1}$$

where  $1 \text{ C s}^{-1} = 1 \text{ A}$

$$\boxed{I = 33.8 \text{ mA}}$$

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**7.2.** After passage of a constant current for 45 min, 7.19 mg of silver (atomic weight =  $107.9 \text{ g mol}^{-1}$ ) was deposited from a solution of silver nitrate. Calculate the current.

**Solution:**

Given:  $t = 45 \text{ min} = 2700 \text{ s}$ ,  $m = 7.19 \text{ mg} = 0.00719 \text{ g}$ ,  $M = 107.9 \text{ g mol}^{-1}$

Required:  $I$

This problem can be solved in a similar manner as problem 7.1, using the expression for current as,  $I = \frac{zF}{t} \left( \frac{m}{M} \right)$ .

The charge on silver in  $\text{AgNO}_3$  is  $\text{Ag}^+$ , therefore  $z = 1$

$$I = \frac{1 \times 96\,485 \text{ C mol}^{-1}}{2700 \text{ s}} \left( \frac{0.00719 \text{ g}}{107.9 \text{ g mol}^{-1}} \right)$$

$$I = 0.002\,381\,241\,7 \text{ C s}^{-1}$$

where  $1 \text{ C s}^{-1} = 1 \text{ A}$

$$\boxed{I = 2.4 \text{ mA}}$$

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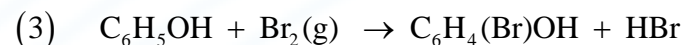
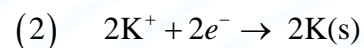
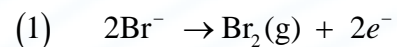
**7.3.** Electrolysis of molten KBr generates bromine gas, which can be used in industrial bromination processes. How long will it take to convert a 500.00-kg batch of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) to monobromophenol using a current of 20 000 A?

**Solution:**

Given:  $m = 500.00 \text{ kg}$ ,  $I = 20\,000 \text{ A}$

Required:  $t$

To solve this problem, we must first outline the chemical reactions that are taking place.



Two moles of electrons are involved in the generation of each mole of bromine gas, which reacts with one mole of phenol, therefore  $z = 2$ .

Each batch consists of 500.00 kg of phenol therefore converting to the number of moles and we can determine the time required to convert all 500.00 kg of phenol into monobromophenol.

Using Eq. 7.6 and  $Q = zF\left(\frac{m}{M}\right)$  from problem 6.1, we can solve for  $t$ ,

$$t = \frac{Q}{I}$$

$$t = \frac{zF}{I} \left( \frac{m}{M} \right)$$

$$M_{\text{C}_6\text{H}_5\text{OH}} = 6(12.011 \text{ g mol}^{-1}) + 6(1.00794 \text{ g mol}^{-1}) + 15.9994 \text{ g mol}^{-1}$$

$$M_{\text{C}_6\text{H}_5\text{OH}} = 94.11304 \text{ g mol}^{-1}$$

$$t = \frac{2 \times 96485 \text{ C mol}^{-1}}{20000 \text{ A}} \left( \frac{500.00 \times 10^3 \text{ g}}{94.11304 \text{ g mol}^{-1}} \right)$$

where  $1 \text{ C s}^{-1} = 1 \text{ A}$

$$t = 51260.16544 \text{ s} \times \frac{1 \text{ h}}{3600 \text{ s}}$$

$$t = 14.23893484 \text{ h}$$

$$\boxed{t = 14.239 \text{ h}}$$

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**7.4.** The following are the molar conductivities  $\Lambda$  of chloroacetic acid in aqueous solution at 25 °C and at various concentrations  $c$ :

$\frac{c}{10^{-4} M}$	625	312.5	156.3	78.1	39.1	19.6	9.8
$\frac{\Lambda}{\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$	53.1	72.4	96.8	127.7	164.0	205.8	249.2

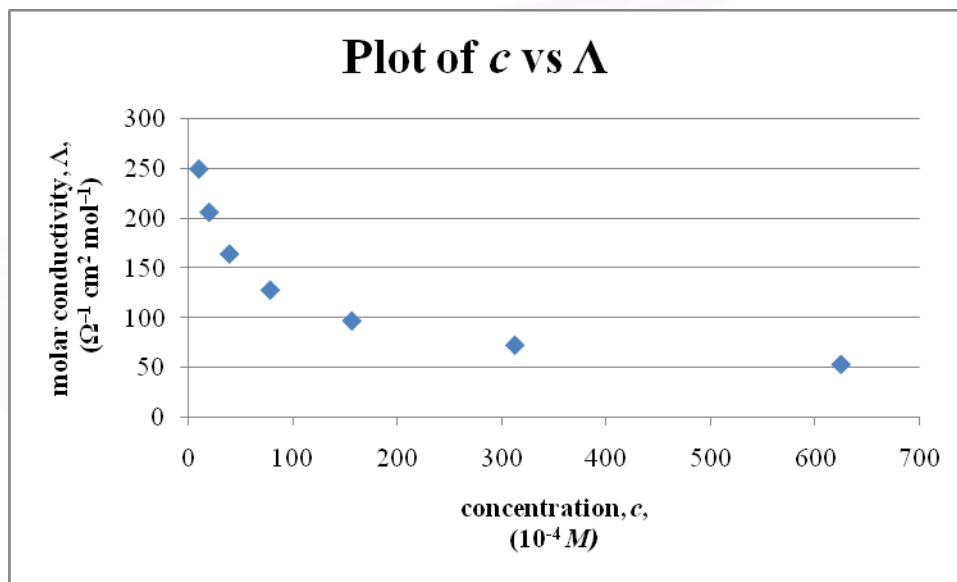
Plot  $\Lambda$  against  $c$ . If  $\Lambda^\circ = 362 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , are these values in accord with the Ostwald Dilution Law? What is the value of the dissociation constant? (See also Problem 7.11.)

**Solution:**

Given:  $c$ ,  $\Lambda$ ,  $\Lambda^\circ = 362 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Required: plot of  $\Lambda$  against  $c$ , are these values in accord with the Ostwald Dilution Law,  $K$

Using the data above, we can create the following plot of  $\Lambda$  against  $c$ .



The Ostwald dilution law is given by Eq. 7.20 as:

$$K = \frac{c(\Lambda/\Lambda^\circ)^2}{1 - (\Lambda/\Lambda^\circ)}$$

To determine if the data given above follows the Ostwald Dilution Law, we see if we can calculate a fixed value for  $K$ , the dissociation constant of the solution.

The results are plotted in the table below.

$c$ $10^{-4} M$	$\Lambda$ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$K$ $M$
625	53.1	0.001575951
312.5	72.4	0.0015625
156.3	96.8	0.001525554
78.1	127.7	0.001501592
39.1	164	0.001467205
19.6	205.8	0.001468105
9.8	249.2	0.001490406

Since the values of  $K$  are reasonably constant, we can say that data given above follows the Ostwald Dilution Law.

The value of the dissociation constant,  $K$ , can be calculated from the average of the  $K$  values obtained above.

$$K_{\text{average}} = 0.001513045 M$$

$$K_{\text{average}} = 1.5 \times 10^{-3} M$$

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**7.5.** The electrolytic conductivity of a saturated solution of silver chloride, AgCl, in pure water at 25 °C is  $1.26 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  higher than that for the water used. Calculate the solubility of AgCl in water if the molar ionic conductivities are  $\text{Ag}^+$ ,  $61.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ;  $\text{Cl}^-$ ,  $76.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

**Solution:**

Given:  $\Delta\kappa = 1.26 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ ,  $\lambda_{\text{Ag}^+} = 61.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ,  $\lambda_{\text{Cl}^-} = 76.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Required: solubility

The expression for molar conductivity is given by Eq. 7.9.

$$\Lambda = \frac{\kappa}{c}$$

In order to solve this problem we can use the concentration as a measure of solubility.

$$\text{solubility} = \frac{\Delta\kappa}{\Lambda_{\text{AgCl}}}$$

$$\Lambda_{\text{AgCl}} = \lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-}$$

$$\text{solubility} = \frac{\Delta\kappa}{\lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-}}$$

$$\text{solubility} = \frac{1.26 \times 10^{-6} \cancel{\Omega^{-1}} \text{ cm}^{-1}}{61.9 \cancel{\Omega^{-1}} \text{ cm}^2 \text{ mol}^{-1} + 76.4 \cancel{\Omega^{-1}} \text{ cm}^2 \text{ mol}^{-1}}$$

$$\text{solubility} = 9.110\,629\,067 \times 10^{-9} \text{ mol cm}^{-3}$$

$$\text{solubility} = 9.110\,629\,067 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\boxed{\text{solubility} = 9.11 \times 10^{-6} \text{ mol dm}^{-3}}$$

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**7.6.** The electrolytic conductivity of a 0.001  $M$  solution of  $\text{Na}_2\text{SO}_4$  is  $2.6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ . If the solution is saturated with  $\text{CaSO}_4$ , the conductivity becomes  $7.0 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ . Calculate the solubility product for  $\text{CaSO}_4$  using the following molar conductivities at these concentrations:

$$\lambda(\text{Na}^+) = 50.1 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}; \lambda\left(\frac{1}{2}\text{Ca}^{2+}\right) = 59.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}.$$

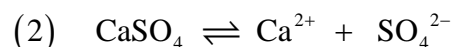
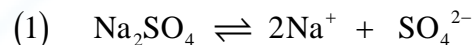
**Solution:**

$$\text{Given: } c_{\text{Na}_2\text{SO}_4} = 0.001 M, \kappa_{\frac{1}{2}\text{Na}_2\text{SO}_4} = 2.6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}, \kappa_{\frac{1}{2}\text{CaSO}_4} = 7.0 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$$

$$\lambda(\text{Na}^+) = 50.1 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}, \lambda\left(\frac{1}{2}\text{Ca}^{2+}\right) = 59.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

Required:  $K_s$  for  $\text{CaSO}_4$

To determine the base dissociation constant for  $\text{CaSO}_4$ , we must first realize which chemical reactions are taking place.



The solubility product is therefore given by:

$$K_s = [\text{Ca}^{2+}][\text{SO}_4^{2-}],$$

To determine the concentrations of the species in the solution, we will determine the electrolytic and molar conductivities.

We are given that the initial electrolytic conductivity of the  $\text{Na}_2\text{SO}_4$  solution is  $2.6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$  which is raised to  $7.0 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$  upon saturation with  $\text{CaSO}_4$ . This means the increase in electrolytic conductivity is:

$$\Delta\kappa = 7.0 \times 10^{-4} \Omega^{-1} \text{cm}^{-1} - 2.6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$$

$$\Delta\kappa = 4.4 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$$

The molar conductivity of the  $\frac{1}{2}\text{CaSO}_4$  solution can be calculated using Eq. 7.9.

$$\Lambda = \frac{\kappa}{c}$$

$$\Lambda_{\frac{1}{2}\text{CaSO}_4} = \frac{\Delta\kappa}{2c}$$

where  $c$  is the concentration of  $\text{CaSO}_4$  and  $2c$  is the concentration of  $\frac{1}{2}\text{CaSO}_4$ .

The molar conductivity of the  $\frac{1}{2}\text{Na}_2\text{SO}_4$  solution is:

$$\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} = \frac{\kappa_{\frac{1}{2}\text{Na}_2\text{SO}_4}}{2c}$$

$$\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} = \frac{2.6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}}{2(0.001 \times 10^{-3} \text{mol cm}^{-3})}$$

$$\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} = 130 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

The molar conductivity of the  $\frac{1}{2}\text{Na}_2\text{SO}_4$  is the same as,

$$\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} = \lambda_{\text{Na}^+} + \lambda_{\frac{1}{2}\text{SO}_4^{2-}}$$

Therefore we can solve for  $\lambda_{\frac{1}{2}\text{SO}_4^{2-}}$  to calculate the molar conductivity of the  $\frac{1}{2}\text{CaSO}_4$ .

$$\lambda_{\frac{1}{2}\text{SO}_4^{2-}} = \Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} - \lambda_{\text{Na}^+}$$

$$\lambda_{\frac{1}{2}\text{SO}_4^{2-}} = 130 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} - 50.1 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\frac{1}{2}\text{SO}_4^{2-}} = 79.9 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\frac{1}{2}\text{CaSO}_4} = \lambda_{\text{Ca}^{2+}} + \lambda_{\frac{1}{2}\text{SO}_4^{2-}}$$

$$\Lambda_{\frac{1}{2}\text{CaSO}_4} = 59.5 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} + 79.9 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\frac{1}{2}\text{CaSO}_4} = 139.4 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

The concentration of  $\frac{1}{2}\text{CaSO}_4$  is therefore given by:

$$c = \frac{\Delta\kappa}{2\Lambda_{\frac{1}{2}\text{CaSO}_4}}$$

$$c = \frac{4.4 \times 10^{-4} \, \cancel{\Omega^{-1}} \text{ cm}^{-1}}{2(139.4 \, \cancel{\Omega^{-1}} \text{ cm}^2 \text{ mol}^{-1})}$$

$$c = 1.578192253 \times 10^{-6} \text{ mol cm}^{-3}$$

$$c = 1.578192253 \times 10^{-3} \text{ mol dm}^{-3}$$

Solving for  $K_s$ ,

$$[\text{Ca}^{2+}] = c$$

$$[\text{SO}_4^{2-}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3} + c$$

The concentration of  $\text{SO}_4^{2-}$  is influenced by the contributions of  $\frac{1}{2}\text{CaSO}_4$  and  $\frac{1}{2}\text{Na}_2\text{SO}_4$ .

$$K_s = c(1.0 \times 10^{-3} \text{ mol dm}^{-3} + c)$$

$$K_s = 4.068\,883\,038 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$$

$$\boxed{K_s = 4.07 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}}$$

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**7.7.** The quantity  $l/A$  of a conductance cell (see Eq. 7.8) is called the cell constant. Find the cell constant for a conductance cell in which the conductance,  $G$ , of a  $0.100\text{ M}$  KCl solution is  $0.01178\text{ S}$  at  $25\text{ }^{\circ}\text{C}$ . The equivalent conductance for  $0.100\text{ M}$  KCl at  $25\text{ }^{\circ}\text{C}$  is  $128.96\text{ S cm}^2\text{ mol}^{-1}$ . If a  $0.0500\text{ M}$  solution of an electrolyte has a measured conductance of  $0.00824\text{ S}$  using this cell, what is the equivalent conductance of the electrolyte?

**Solution:**

Given:  $G = 0.01178\text{ S}$ ,  $T = 25\text{ }^{\circ}\text{C}$ ,  $\Lambda = 128.96\text{ S cm}^2\text{ mol}^{-1}$  at  $c_{\text{KCl}} = 0.100\text{ M}$

$$G = 0.00824\text{ S}, c_{\text{electrolyte}} = 0.0500\text{ M}$$

Required:  $l/A$ ,  $\Lambda_{\text{electrolyte}}$

In order to determine the cell constant, we must first calculate the value for the electrolytic conductance. As we know, this can be obtained using Eq. 7.9.

$$\Lambda = \frac{\kappa}{c}$$

$$\kappa = c\Lambda$$

$$\kappa = (0.100 \times 10^{-3} \cancel{\text{mol cm}^{-3}}) (128.96\text{ S cm}^2 \cancel{\text{mol}^{-1}})$$

$$\kappa = 0.012896\text{ S cm}^{-1}$$

We can now use Eq. 7.8 to solve for the cell constant,  $l/A$ .

$$G(\text{conductance}) = \kappa \frac{A}{l}$$

$$\frac{l}{A} = \frac{\kappa}{G}$$

$$\frac{l}{A} = \frac{0.012896 \cancel{\text{S}} \text{ cm}^{-1}}{0.01178 \cancel{\text{S}}}$$

$$\frac{l}{A} = 1.094\,736\,842 \text{ cm}^{-1}$$

$$\boxed{\frac{l}{A} = 1.09 \text{ cm}^{-1}}$$

The equivalent conductance of the electrolyte in this same cell can be found using the cell constant calculated above and solve for  $\Lambda$  from Eq. 7.9.

$$\Lambda = \frac{\kappa}{c}$$

$$\kappa = G \frac{l}{A}$$

$$\Lambda_{\text{electrolyte}} = \frac{G \frac{l}{A}}{c_{\text{electrolyte}}}$$

$$\Lambda_{\text{electrolyte}} = \frac{(0.00824 \text{ S})(1.094\,736\,842 \text{ cm}^{-1})}{0.0500 \times 10^{-3} \text{ mol cm}^{-3}}$$

$$\Lambda_{\text{electrolyte}} = 180.412\,631\,6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\boxed{\Lambda_{\text{electrolyte}} = 180 \text{ S cm}^2 \text{ mol}^{-1}}$$

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**7.8.** A conductivity cell when standardized with 0.01 M KCl was found to have a resistance of 189  $\Omega$ . With 0.01 M ammonia solution the resistance was 2460  $\Omega$ . Calculate the base dissociation constant of ammonia, given the following molar conductivities at these concentrations:  $\lambda(\text{K}^+) = 73.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ;  $\lambda(\text{Cl}^-) = 76.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ;  $\lambda(\text{NH}_4^+) = 73.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ;  $\lambda(\text{OH}^-) = 198.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

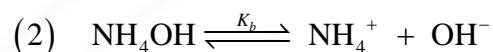
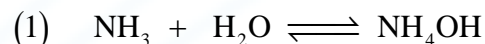
**Solution:**

Given:  $c_{\text{KCl}} = 0.01 \text{ M}$ ,  $R = 189 \Omega$ ,  $c_{\text{NH}_3} = 0.01 \text{ M}$ ,  $R = 2460 \Omega$

$$\lambda(\text{K}^+) = 73.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, \lambda(\text{Cl}^-) = 76.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, \lambda(\text{NH}_4^+) = 73.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, \lambda(\text{OH}^-) = 198.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Required:  $K_b$

In order to determine the base dissociation constant for ammonia, we must first outline which chemical reactions are taking place.



The base dissociation constant is therefore given by:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

To solve for the concentrations of each species, we may begin by calculating the value for the electrolytic conductance of the standard KCl

$$\Lambda = \frac{\kappa}{c}$$

$$\kappa = c\Lambda$$

$$\Lambda_{\text{KCl}} = \lambda_{\text{K}^+} + \lambda_{\text{Cl}^-}$$

solution in the cell.  $\Lambda_{\text{KCl}} = 73.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} + 76.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

$$\Lambda_{\text{KCl}} = 149.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\kappa_{\text{KCl}} = (0.01 \times 10^{-3} \text{ mol cm}^{-3}) (149.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$$

$$\kappa_{\text{KCl}} = 0.001499 \Omega^{-1} \text{ cm}^{-1}$$

Recall that the resistance is inversely proportional to the conductance. The electrolytic conductivity of the ammonia solution is therefore,

$$\kappa_{\text{NH}_3} = \kappa_{\text{KCl}} \times \frac{R_{\text{KCl}}}{R_{\text{NH}_3}}$$

$$\kappa_{\text{NH}_3} = 0.001\,499\,\Omega^{-1}\,\text{cm}^{-1} \times \frac{189\,\cancel{\Omega}}{2460\,\cancel{\Omega}}$$

$$\kappa_{\text{NH}_3} = 1.151\,670\,732 \times 10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$$

The molar conductivity of  $\text{NH}_4^+ + \text{OH}^-$  is:

$$\Lambda_{\text{NH}_4\text{OH}} = \lambda_{\text{NH}_4^+} + \lambda_{\text{OH}^-}$$

$$\Lambda_{\text{NH}_4\text{OH}} = 73.4\,\Omega^{-1}\,\text{cm}^2\text{mol}^{-1} + 198.6\,\Omega^{-1}\,\text{cm}^2\text{mol}^{-1}$$

$$\Lambda_{\text{NH}_4\text{OH}} = 272\,\Omega^{-1}\,\text{cm}^2\text{mol}^{-1}$$

Using Eq. 7.9, we can calculate the concentrations of  $\text{NH}_4^+$  and  $\text{OH}^-$ .

$$\Lambda = \frac{\kappa}{c}$$

$$c = \frac{\kappa_{\text{NH}_3}}{\Lambda_{\text{NH}_4\text{OH}}}$$

$$c = \frac{1.151\,670\,732 \times 10^{-4}\,\cancel{\Omega^{-1}}\,\text{cm}^{-1}}{272\,\cancel{\Omega^{-1}}\,\text{cm}^2\text{mol}^{-1}}$$

$$c = 4.234\,083\,572 \times 10^{-7}\,\text{mol cm}^{-3}$$

$$c = 4.234\,083\,572 \times 10^{-4}\,\text{mol dm}^{-3}$$

Knowing that;  $c = [\text{NH}_4^+] = [\text{OH}^-]$ , we can solve for  $K_b$ .

	$\text{NH}_4\text{OH}$	$\rightleftharpoons$	$\text{NH}_4^+$	+	$\text{OH}^-$	
$C_{\text{initial}}$	0.01		0		0	$\text{mol dm}^{-3}$
$C_{\text{equilibrium}}$	$0.01 - c$		$c$		$c$	$\text{mol dm}^{-3}$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{c^2}{0.01 - c}$$

$$K_b = \frac{(4.234\,083\,572 \times 10^{-4} \text{ mol dm}^{-3})^2}{0.01 - 4.234\,083\,572 \times 10^{-4} \text{ mol dm}^{-3}}$$

$$K_b = 1.872\,008\,786 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\boxed{K_b = 1.9 \times 10^{-5} \text{ mol dm}^{-3}}$$

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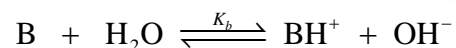
**7.9.** The conductivity of a 0.0312 M solution of a weak base is  $1.53 \times 10^{-4} \text{ S cm}^{-1}$ . If the sum of the limiting ionic conductances for  $\text{BH}^+$  and  $\text{OH}^-$  is  $237.0 \text{ S cm}^2 \text{ mol}^{-1}$ , what is the value of the base constant  $K_b$ ?

**Solution:**

Given:  $c = 0.0312 \text{ M}$ ,  $\kappa = 1.53 \times 10^{-4} \text{ S cm}^{-1}$ ,  $\Lambda^\circ = 237.0 \text{ S cm}^2 \text{ mol}^{-1}$

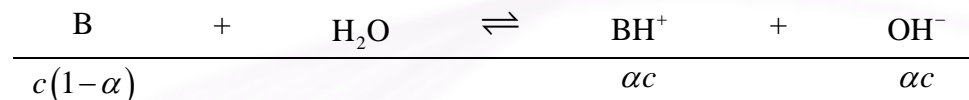
Required:  $K_b$

In order to determine the base dissociation constant for the solution, we must write out the chemical reaction that is taking place.



Since we are told we have a weak base, it is possible to apply Ostwald's Dilution Law and introduce the degree of dissociation,  $\alpha$ , given by Eq. 7.11.

$$\alpha = \frac{\Lambda}{\Lambda^\circ}$$



The base dissociation constant is therefore given by Eq. 7.18.

$$K_b = \frac{c\alpha^2}{1-\alpha}$$

And the degree of dissociation is determined by calculating the molar conductivity of  $\text{B} + \text{H}_2\text{O}$  using Eq. 7.9.

$$\Lambda = \frac{\kappa}{c}$$

$$\Lambda = \frac{1.53 \times 10^{-4} \text{ S cm}^{-1}}{0.0312 \times 10^{-3} \text{ mol cm}^{-3}}$$

$$\Lambda = 4.903846154 \text{ S cm}^2 \text{ mol}^{-1}$$

The degree of dissociation is therefore,

$$\alpha = \frac{4.903\,846\,154 \cancel{\text{ S cm}^2 \text{ mol}^{-1}}}{237.0 \cancel{\text{ S cm}^2 \text{ mol}^{-1}}}$$

$$\alpha = 0.020\,691\,334$$

Solving for  $K_b$ , we obtain the following:

$$K_b = \frac{(0.0312 \text{ mol dm}^{-3})(0.020\,691\,334)^2}{1 - 0.020\,691\,334}$$

$$K_b = 1.363\,992\,486 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\boxed{K_b = 1.36 \times 10^{-5} \text{ mol dm}^{-3}}$$

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**7.10.** The equivalent conductance of KBr solutions as a function of concentration at 25 °C is given in the following table. By a linear regression analysis of suitable variables, find the value of  $\Lambda^\circ$  for KBr.

$c/10^{-3} M$	0.25	0.36	0.50	0.75	1.00	1.60	2.00	5.00	10.00
$\Lambda/\text{S cm}^2 \text{mol}^{-1}$	150.16	149.87	149.55	149.12	148.78	148.02	147.64	145.47	143.15

**Solution:**

Given:  $T = 25^\circ\text{C}$ , data given above

Required:  $\Lambda^\circ_{\text{KBr}}$

The relationship between  $\Lambda$  and  $c$  is given by the Debye-Hückel-Onsager Equation, Eq. 7.53.

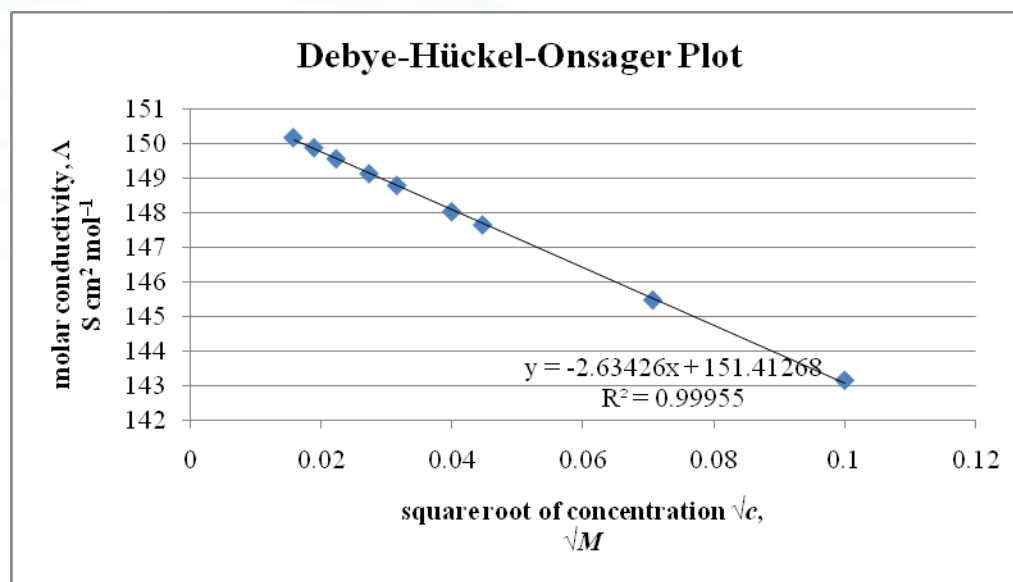
$$\Lambda = \Lambda^\circ - (P + Q\Lambda^\circ)\sqrt{c}$$

In order to solve for  $\Lambda^\circ_{\text{KBr}}$ , we can plot  $\sqrt{c}$  against  $\Lambda$ , where  $\sqrt{c} = \sqrt{c \times 10^{-3}}$

$\sqrt{c} (\sqrt{M})$	$\Lambda (\text{S cm}^2 \text{mol}^{-1})$
0.01581139	150.16
0.01897367	149.87
0.02236068	149.55
0.02738613	149.12
0.03162278	148.78
0.04	148.02
0.04472136	147.64
0.07071068	145.47

0.1

143.15



From the linear regression, the y- intercept will be the value of  $\Lambda_{KBr}^\circ$

$$\Lambda_{KBr}^\circ = 151.41268\ S\ cm^2\ mol^{-1}$$

$$\boxed{\Lambda_{KBr}^\circ = 151.41\ S\ cm^2\ mol^{-1}}$$

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**7.11.** Equation 7.20 is one form of Ostwald's dilution law. Show how it can be linearized (i.e., convert it into a form that will allow experimental values of  $\Lambda$  at various concentrations to be tested by means of a straight-line plot). Explain how  $\Lambda^\circ$  and  $K$  can be obtained from the plot.

Kraus and Callis, *J. Amer. Chem. Soc.*, 45, 2624(1923), obtained the following electrolytic conductivities  $\kappa$  for the dissociation of tetramethyl tin chloride,  $(\text{CH}_3)_4\text{SnCl}$ , in ethyl alcohol solution at 25.0 °C and at various concentrations  $c$ :

$c/10^{-4} \text{ mol dm}^{-3}$	1.566	2.600	6.219	10.441
$\kappa/10^{-6} \Omega^{-1} \text{ cm}^{-1}$	1.788	2.418	4.009	5.336

By the use of the linear plot you have devised, determine  $\Lambda^\circ$  and  $K$ .

**Solution:**

Given:  $T = 25^\circ\text{C}$ , data above

Required:  $\Lambda^\circ$ ,  $K$

Ostwald's dilution law, given by Eq. 7.20 can be linearized in the following manner:

$$K = \frac{c(\Lambda/\Lambda^\circ)^2}{1 - (\Lambda/\Lambda^\circ)}$$

$$K(1 - (\Lambda/\Lambda^\circ)) = c(\Lambda/\Lambda^\circ)^2$$

$$c = \frac{K - K(\Lambda/\Lambda^\circ)}{(\Lambda/\Lambda^\circ)^2}$$

$$c = \frac{(K - K(\Lambda/\Lambda^\circ))\Lambda^{\circ 2}}{\Lambda^2}$$

$$c = \frac{K\Lambda^{\circ 2} - K\Lambda^\circ \Lambda}{\Lambda^2}$$

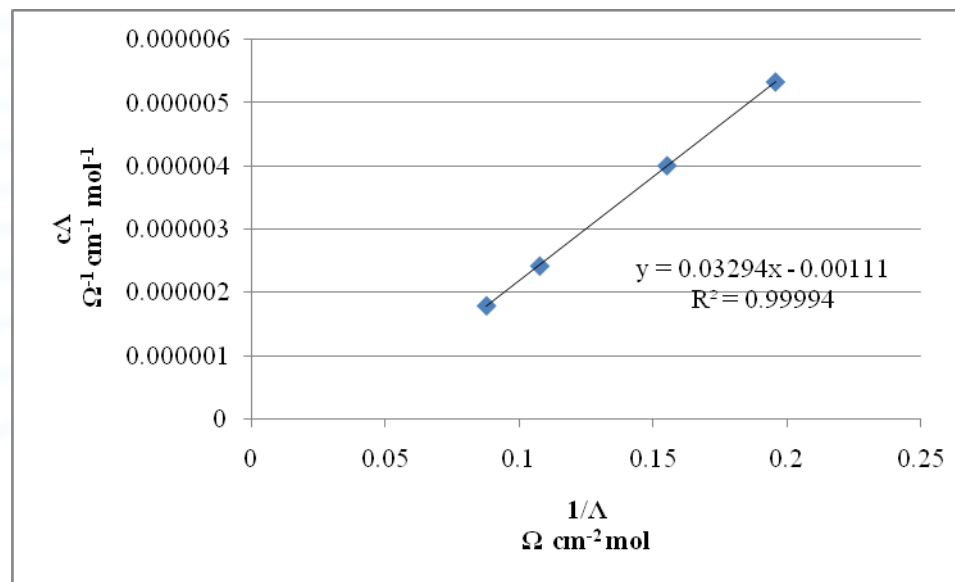
$$c\Lambda = \frac{K\Lambda^{\circ 2}}{\Lambda} - K\Lambda^\circ$$

From here, we can plot  $c\Lambda$  against  $\frac{1}{\Lambda}$  and determine  $\Lambda^\circ$  and  $K$ .

We can calculate  $\Lambda$  from Eq. 7.9 at each concentration given.  $\Lambda = \frac{K}{c}$ . This leads to a table of values with the following:

$c$ $10^{-4} \text{ mol dm}^{-3}$	$\kappa$ $10^{-6} \Omega^{-1} \text{ cm}^{-1}$	$\Lambda$ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$c\Lambda$ $\Omega^{-1} \text{ cm}^{-1}$	$1/\Lambda$ $\Omega \text{ cm}^{-2} \text{ mol}$
1.566	1.788	11.417625	$1.788 \times 10^{-6}$	0.087584
2.6	2.418	9.3	$2.418 \times 10^{-6}$	0.107527
6.219	4.009	6.446374	$4.009 \times 10^{-6}$	0.155126
10.441	5.336	5.1106216	$5.336 \times 10^{-6}$	0.195671

Now we obtain the following graph:



From the linear regression, the y- intercept will be  $K\Lambda^\circ$  and the slope will be  $K\Lambda^{\circ 2}$



$$K\Lambda^\circ = 0.00111 \Omega^{-1} \text{ cm}^{-1}$$

$$K\Lambda^{\circ 2} = 0.03294 \Omega^{-2} \text{ cm mol}^{-1}$$

$$\Lambda^\circ = \frac{K\Lambda^{\circ 2}}{K\Lambda^\circ}$$

$$\Lambda^\circ = \frac{0.03294 \Omega^{-2} \text{ cm mol}^{-1}}{0.00111 \Omega^{-1} \text{ cm}^{-1}}$$

$$\Lambda^\circ = 29.675\,675\,68 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\boxed{\Lambda^\circ = 30 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$$

$$K = \frac{0.00111 \Omega^{-1} \text{ cm}^{-1}}{\Lambda^\circ}$$

$$K = \frac{0.00111 \cancel{\Omega^{-1}} \text{ cm}^{-1}}{29.675\,675\,68 \cancel{\Omega^{-1}} \text{ cm}^2 \text{ mol}^{-1}}$$

$$K = 3.740\,437\,158 \times 10^{-5} \text{ mol cm}^{-3}$$

$$\boxed{K = 3.7 \times 10^{-2} \text{ mol dm}^{-3}}$$

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**7.12.** A certain chemical company wishes to dispose of its acetic acid waste into a local river by first diluting it with water to meet the regulation that the total acetic acid concentration cannot exceed 1500 ppm by weight. You are asked to design a system using conductance to continuously monitor the acid concentration in the water and trigger an alarm if the 1500 ppm limit is exceeded. What is the maximum conductance at which the system should trigger an alarm at a constant temperature of 25 °C? (Assume that the cell constant is 1.0 cm<sup>-1</sup> and that the density of 1500 ppm acetic acid solution is not appreciably different from that of pure water. The  $\Lambda^\circ$  for acetic acid is 390.7 S cm<sup>2</sup> mol<sup>-1</sup> and  $K_a = 1.81 \times 10^{-5}$  mol dm<sup>-3</sup> at 25 °C. Ignore the conductance of water.)

**Solution:**

Given:  $c_{\max} = 1500$  ppm,  $\frac{A}{l} = 1.0$  cm<sup>-1</sup>,  $\rho_{\text{acetic acid}} \approx \rho_{\text{water}}$ ,  $\Lambda^\circ = 390.7$  S cm<sup>2</sup> mol<sup>-1</sup>,  $K_a = 1.81 \times 10^{-5}$  mol dm<sup>-3</sup>

$$T = 25 \text{ }^\circ\text{C}$$

Required:  $G$

In order to solve this problem, we must first convert the concentration from parts per million to SI units.

$$c = 1500 \text{ ppm} = \frac{1500 \text{ g acid}}{10^6 \text{ g solution}}$$

$$c = \frac{1.500 \text{ g acid}}{1000 \text{ g solution}}$$

$$M_{\text{acetic acid}} = 2(12.011 \text{ g mol}^{-1}) + 4(1.00794 \text{ g mol}^{-1}) + 2(15.9994 \text{ g mol}^{-1})$$

$$M_{\text{acetic acid}} = 60.05256 \text{ g mol}^{-1}$$

$$c = \frac{1.500 \cancel{\text{g}} \text{ acid}}{60.05256 \cancel{\text{g}} \text{ mol}^{-1}} \times \frac{1}{1 \text{ kg solution}}$$

$$c = 0.0249781192 \text{ mol kg}^{-1}$$

Since the solution has the same density as water, 1.00 kg of solution has a volume of 1.0 dm<sup>3</sup>. Therefore we can assume the solution has concentration,  $c = 0.0249781192$  M.

The conductance of a solution is given by Eq. 7.8.

$$G(\text{conductance}) = \kappa \frac{A}{l}$$

Since acetic acid is a weak acid, we may use the Ostwald's Dilution Law, Eq. 7.20, to solve for  $\Lambda$ .

$$K = \frac{c(\Lambda/\Lambda^\circ)^2}{1 - (\Lambda/\Lambda^\circ)}$$

$$K - K(\Lambda/\Lambda^\circ) = c(\Lambda/\Lambda^\circ)^2$$

$$K - K(\Lambda/\Lambda^\circ) - c(\Lambda/\Lambda^\circ)^2 = 0$$

To solve for  $\Lambda/\Lambda^\circ$ , we use the quadratic equation.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\Lambda/\Lambda^\circ = \frac{K \pm \sqrt{K^2 - 4(-c)K}}{2(-c)}$$

$$\Lambda/\Lambda^\circ = \frac{K \pm \sqrt{K^2 + 4cK}}{-2c}$$

$$\Lambda/\Lambda^\circ = \frac{1.81 \times 10^{-5} M \pm \sqrt{(1.81 \times 10^{-5} M)^2 + 4(0.0249781192 M)(1.81 \times 10^{-5} M)}}{-2(0.0249781192 M)}$$

$$\Lambda/\Lambda^\circ = 0.026\,939\,569\,1 \text{ and } -0.026\,903\,369\,1$$

We will disregard the negative value and take  $\Lambda/\Lambda^\circ = 0.026\,939\,569\,1$  to solve for  $\Lambda$ .

$$\Lambda = (0.026\,939\,569\,1)(\Lambda^\circ)$$

$$\Lambda = (0.026\,939\,569\,1)(390.7 \text{ S cm}^2 \text{ mol}^{-1})$$

$$\Lambda = 10.525\,289\,64 \text{ S cm}^2 \text{ mol}^{-1}$$

Using Eq. 7.9, we can substitute for the value of  $\kappa$  and determine the conductance of the solution.

$$\Lambda = \frac{\kappa}{c}$$

$$\kappa = c\Lambda$$

$$G = \kappa \frac{A}{l}$$

$$G = (c\Lambda) \frac{A}{l}$$

$$G = (0.024\,978\,119\,2 \text{ mol dm}^{-3}) (10.525\,289\,64 \text{ S cm}^2 \text{ mol}^{-1}) (1.0 \text{ cm})$$

$$G = 0.262\,901\,938\,9 \text{ dm}^{-3} \text{ S cm}$$

$$G = 0.262\,901\,938\,9 \times 10^{-3} \text{ cm}^{-3} \text{ S cm}$$

$$G = 2.629\,019\,389 \times 10^{-4} \text{ S cm}^{-2}$$

$$\boxed{G = 2.63 \times 10^{-4} \text{ S cm}^{-2}}$$

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**7.13.** How far can the conductivity of water at 25 °C be lowered *in theory* by removing impurities? The  $\Lambda^\circ$  (in  $\text{S cm}^2 \text{ mol}^{-1}$ ) for KOH, HCl, and KCl are, respectively, 274.4, 426.04, and 149.86.  $K_w = 1.008 \times 10^{-14}$ . Compare your answer to the *experimental* value of  $5.8 \times 10^{-8} \text{ S cm}^{-1}$  obtained by Kohlrausch and Heydweiller, *Z. phys. Chem.* 14, 317(1894).

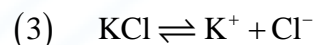
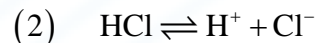
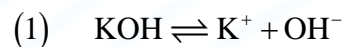
**Solution:**

Given:  $\Lambda_{\text{KOH}}^\circ = 274.4 \text{ S cm}^2 \text{ mol}^{-1}$ ,  $\Lambda_{\text{HCl}}^\circ = 426.04 \text{ S cm}^2 \text{ mol}^{-1}$ ,  $\Lambda_{\text{KCl}}^\circ = 149.86 \text{ S cm}^2 \text{ mol}^{-1}$

$$T = 25 \text{ }^\circ\text{C}, K_w = 1.008 \times 10^{-14}, \kappa_{\text{exp}} = 5.8 \times 10^{-8} \text{ S cm}^{-1}$$

Required:  $\kappa$

The dissociations of each salt in water are given by:



By rearranging we find that,

$$\Lambda_{\text{H}_2\text{O}}^\circ = \Lambda_{\text{KOH}}^\circ + \Lambda_{\text{HCl}}^\circ - \Lambda_{\text{KCl}}^\circ$$

$$\Lambda_{\text{H}_2\text{O}}^\circ = 274.4 \text{ S cm}^2 \text{ mol}^{-1} + 426.04 \text{ S cm}^2 \text{ mol}^{-1} - 149.86 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\text{H}_2\text{O}}^\circ = 550.58 \text{ S cm}^2 \text{ mol}^{-1}$$

In pure water, the only species that conduct electricity are  $\text{H}^+$  and  $\text{OH}^-$  ions. According to  $K_w = [\text{H}^+][\text{OH}^-]$ , each have a concentration of ;

$$\sqrt{K_w} = \sqrt{1.008 \times 10^{-14} \text{ mol dm}^{-3}} = 1.0039992032 \times 10^{-7} \text{ mol dm}^{-3}.$$

Since this concentration is very low, we can assume that  $\Lambda_{\text{H}_2\text{O}} \approx \Lambda_{\text{H}_2\text{O}}^\circ$ .

$$\Lambda = \frac{\kappa}{c}$$

$$\kappa = (1.003\,999\,203\,2 \times 10^{-10} \text{ mol cm}^{-3}) (550.58 \text{ S cm}^2 \text{ mol}^{-1})$$

$$\kappa = 5.527\,779\,329 \times 10^{-8} \text{ S cm}^{-1}$$

$$\boxed{\kappa = 5.528 \times 10^{-8} \text{ S cm}^{-1}}$$

Compared to the experimental value of  $5.8 \times 10^{-8} \text{ S cm}^{-1}$ , the conductivity determined through this process produces a very similar result.

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**7.14.** The radius of the ionic atmosphere ( $1/\kappa$ ) for a univalent electrolyte is 0.964 nm at a concentration of 0.10 M in water at 25 °C ( $\epsilon=78$ ). Estimate the radius (a) in water at a concentration of 0.0001 M and (b) in a solvent of  $\epsilon=38$  at a concentration of 0.10 M.

**Solution:**

Given:  $\frac{1}{\kappa} = 0.964 \text{ nm}$ ,  $c = 0.10 \text{ M}$ ,  $T = 25 \text{ °C}$ ,  $\epsilon = 78$

Required: see above

a) Eq. 7.50 indicates that the thickness of the ionic atmosphere is inversely proportional to the square root of the concentration.

$$\frac{1}{\kappa} = \left( \frac{\epsilon_0 \epsilon k_B T}{e^2 \sum_i c_i z_i^2 L} \right)^{1/2}$$

$$\left( \frac{1}{\kappa} \right) \propto \frac{1}{\sqrt{c}}$$

Therefore the radius in water, where the electrolyte has  $c = 0.0001 \text{ M}$ , can be obtained from the ratio of proportions.

$$\frac{\left(\frac{1}{\kappa}\right)_1}{\sqrt{c_2}} = \frac{\left(\frac{1}{\kappa}\right)_2}{\sqrt{c_1}}$$

$$\left(\frac{1}{\kappa}\right)_2 = \frac{\sqrt{c_1} \left(\frac{1}{\kappa}\right)_1}{\sqrt{c_2}}$$

$$\left(\frac{1}{\kappa}\right)_2 = \sqrt{\frac{c_1}{c_2}} \left(\frac{1}{\kappa}\right)_1$$

$$\left(\frac{1}{\kappa}\right)_2 = \sqrt{\frac{0.1 \cancel{M}}{0.0001 \cancel{M}}} (0.964 \text{ nm})$$

$$\left(\frac{1}{\kappa}\right)_2 = 30.484 \text{ } 356 \text{ } 64 \text{ nm}$$

$$\boxed{\left(\frac{1}{\kappa}\right)_2 = 30.5 \text{ nm}}$$

**b)** Similarly, we see from Eq. 7.50 that the thickness of the ionic atmosphere is proportional to the square root of the permittivity

$$\left(\frac{1}{\kappa}\right) \propto \sqrt{\epsilon}$$

The radius in water where  $\epsilon = 38$ , can be obtained from the ratio of proportions.



$$\left(\frac{1}{\kappa}\right)_2 = \sqrt{\frac{\epsilon_2}{\epsilon_1}} \left(\frac{1}{\kappa}\right)_1$$

$$\left(\frac{1}{\kappa}\right)_2 = \sqrt{\frac{38}{78}} (0.964 \text{ nm})$$

$$\left(\frac{1}{\kappa}\right)_2 = 0.672\,855\,072\,6 \text{ nm}$$

$$\boxed{\left(\frac{1}{\kappa}\right)_2 = 0.673 \text{ nm}}$$

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- 7.15.** The molar conductivities of 0.001 M solutions of potassium chloride, sodium chloride, and potassium sulfate  $\left(\frac{1}{2}\text{K}_2\text{SO}_4\right)$  are 149.9, 126.5, and  $153.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively. Calculate an approximate value for the molar conductivity of a solution of sodium sulfate of the same concentration.

**Solution:**

Given:  $c = 0.001 \text{ M}$

$$\Lambda_{\text{KCl}} = 149.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, \Lambda_{\text{NaCl}} = 126.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, \Lambda_{\frac{1}{2}\text{K}_2\text{SO}_4} = 153.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Required:  $\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4}$

The molar conductivity of  $\frac{1}{2}\text{Na}_2\text{SO}_4$  is given by the combination of the molar conductivities of each salt. We must also subtract the molar conductivity of KCl since we are considering the solution containing only sodium and sulfate ions.

$$\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} = \Lambda_{\text{NaCl}} + \Lambda_{\frac{1}{2}\text{K}_2\text{SO}_4} - \Lambda_{\text{KCl}}$$

$$\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} = 126.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} + 153.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} - 149.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\boxed{\Lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4} = 129.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$$

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**7.16.** The molar conductivity at 18 °C of a 0.0100 M aqueous solution of ammonia is  $9.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . For  $\text{NH}_4\text{Cl}$ ,  $\Lambda^\circ = 129.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and the molar ionic conductivities of  $\text{OH}^-$  and  $\text{Cl}^-$  are 174.0 and  $65.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively. Calculate  $\Lambda^\circ$  for  $\text{NH}_3$  and the degree of ionization in 0.01 M solution.

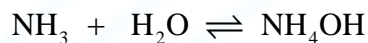
**Solution:**

Given:  $T = 18^\circ\text{C}$ ,  $c_{\text{NH}_3} = 0.0100 \text{ M}$ ,  $\Lambda_{\text{NH}_3} = 9.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ,  $\Lambda_{\text{NH}_4\text{Cl}}^\circ = 129.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ,

$$\lambda_{\text{OH}^-}^\circ = 174.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, \lambda_{\text{Cl}^-}^\circ = 65.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, c = 0.01 \text{ M}$$

Required:  $\Lambda_{\text{NH}_3}^\circ, \alpha$

In solution, ammonia reacts in following manner,



As a result, we can obtain  $\Lambda_{\text{NH}_3}^\circ$  from the molar conductivity of  $\text{NH}_4\text{OH}$ .

$$\Lambda_{\text{NH}_4\text{OH}}^\circ = \Lambda_{\text{NH}_4\text{Cl}}^\circ + \lambda_{\text{OH}^-}^\circ - \lambda_{\text{Cl}^-}^\circ$$

$$\Lambda_{\text{NH}_4\text{OH}}^\circ = 129.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} + 174.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} - 65.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\text{NH}_4\text{OH}}^\circ = 238.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\boxed{\Lambda_{\text{NH}_4\text{OH}}^\circ = 238 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$$

The degree of dissociation is defined by Eq. 7.11 which states,

$$\alpha = \frac{\Lambda}{\Lambda^\circ}$$

$$\alpha = \frac{9.6 \cancel{\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}}{238.2 \cancel{\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}}$$

$$\alpha = 0.040\,302\,267$$

$$\boxed{\alpha = 4.0 \times 10^{-2}}$$

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**7.17.** A solution of LiCl was electrolyzed in a Hittorf cell. After a current of 0.79 A had been passed for 2 h, the mass of LiCl in the anode compartment had decreased by 0.793 g.

a. Calculate the transport numbers of the  $\text{Li}^+$  and  $\text{Cl}^-$  ions.

b. If  $\Lambda^\circ(\text{LiCl})$  is  $115.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , what are the molar ionic conductivities and the ionic mobilities?

**Solution:**

Given:  $I = 0.79 \text{ A}$ ,  $t = 2 \text{ h}$ ,  $\Delta m = 0.793 \text{ g}$ ,  $\Lambda_{\text{LiCl}}^\circ = 115.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Required: see above

a) To solve this problem, we can use the Hittorf method. This method gives the transport numbers according to Eq. 7.75 and Eq. 7.76.

$$\frac{\text{amount lost from anode compartment}}{\text{amount deposited}} = t_+ \quad \text{And} \quad \frac{\text{amount lost from cathode compartment}}{\text{amount deposited}} = t_-$$

We will use the number of moles to measure the amounts of the  $\text{Li}^+$  and  $\text{Cl}^-$  ions. To determine the total amount deposited, we use Eq. 7.6.

$$Q = It$$

$$Q = (0.79 \text{ A}) \left( 2 \text{ h} \times 3600 \frac{\text{s}}{\text{h}} \right)$$

$$Q = 5688 \text{ A s}$$

$$Q = 5688 \text{ C}$$

In problem 7.1 we found that  $Q = zFn$  since the charge carried by 1 mol of ions bearing  $z$  unit charges is  $zF$ , where  $1 F = 96485 \text{ C mol}^{-1}$ . Solving for  $n$ , we can determine the total amount deposited.

$$n = \frac{Q}{zF}$$

$$\text{amount deposited} = \frac{5688 \text{ C}}{(1)(96485 \text{ C mol}^{-1})}$$

$$\text{amount deposited} = 0.0589521687 \text{ mol}$$

The amount lost of LiCl lost in the anode compartment is given by  $n_{\text{Cl}}$ .

$$n_{\text{LiCl}} = \frac{m_{\text{LiCl}}}{M_{\text{LiCl}}}$$

$$M_{\text{LiCl}} = 6.941 \text{ g mol}^{-1} + 35.4527 \text{ g mol}^{-1}$$

$$M_{\text{LiCl}} = 42.3927 \text{ g mol}^{-1}$$

$$n_{\text{LiCl}} = \frac{0.793 \cancel{\text{ g}}}{42.3927 \cancel{\text{ g}} \text{ mol}^{-1}}$$

$$n_{\text{LiCl}} = 0.018\,705\,609\,6 \text{ mol}$$

The anode reaction that is occurring is  $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + e^-$ , therefore  $0.058\,952\,168\,7 \text{ mol}$  of  $\text{Cl}^-$  are removed by electrolysis. The amount lost from the anode compartment is given by,  $n_{\text{net}} = n_{\text{total}} - n_{\text{LiCl}}$

$$n_{\text{net}} = 0.058\,952\,168\,7 \text{ mol} - 0.018\,705\,609\,6 \text{ mol}$$

$$n_{\text{net}} = 0.040\,246\,559\,2 \text{ mol}$$

Solving for  $t_{\text{Cl}^-}$  we obtain,

$$t_+ = t_{\text{Cl}^-} = \frac{0.040\,246\,559\,2 \cancel{\text{ mol}}}{0.058\,952\,168\,7 \cancel{\text{ mol}}}$$

$$t_{\text{Cl}^-} = 0.682\,698\,534$$

$$\boxed{t_{\text{Cl}^-} = 0.68}$$

The second transport number is given by  $1 - t_+$ ,

$$t_- = t_{\text{Li}^+} = 1 - t_+$$

$$t_{\text{Li}^+} = 1 - 0.682\,698\,534$$

$$t_{\text{Li}^+} = 0.317\,301\,466$$

$$\boxed{t_{\text{Li}^+} = 0.32}$$

b) In order to determine the molar ionic conductivities we will use Eq. 7.79 which states,

$$t_+ = \frac{\lambda_+^\circ}{\Lambda^\circ} \text{ and } t_- = \frac{\lambda_-^\circ}{\Lambda^\circ}$$

To solve, we rearrange and use  $\Lambda_{\text{LiCl}}^\circ = 115.0 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

$$\lambda_{\text{Cl}^-}^\circ = \Lambda^\circ t_{\text{Cl}^-}$$

$$\lambda_{\text{Cl}^-}^\circ = (115.0 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})(0.682 \, 698 \, 534)$$

$$\lambda_{\text{Cl}^-}^\circ = 78.510 \, 331 \, 41 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\boxed{\lambda_{\text{Cl}^-}^\circ = 79 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$$

$$\lambda_{\text{Li}^+}^\circ = \Lambda^\circ t_{\text{Li}^+}$$

$$\lambda_{\text{Li}^+}^\circ = (115.0 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})(0.317 \, 301 \, 466)$$

$$\lambda_{\text{Li}^+}^\circ = 36.489 \, 668 \, 59 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\boxed{\lambda_{\text{Li}^+}^\circ = 36 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$$

The ionic mobility is given in terms of molar ionic conductivity by Eq. 7.64.

$$\lambda_+^\circ = \frac{\kappa_+}{c_+} = F u_+$$

$$u_+ = \frac{\lambda_+^\circ}{F}$$

$$u_{\text{Cl}^-} = \frac{78.510\,331\,41\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}}{96\,485\,\text{C}}$$

$$u_{\text{Cl}^-} = 8.137\,050\,465 \times 10^{-4}\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}\,\text{C}^{-1}$$

where  $1\,\Omega^{-1} = 1\,\text{A}\,\text{V}^{-1}$  and  $1\,\text{A} = 1\,\text{C}\,\text{s}^{-1}$

therefore,  $1\,\Omega^{-1} = 1\,\text{C}\,\text{s}^{-1}\,\text{V}^{-1}$

$$u_{\text{Cl}^-} = 8.137\,050\,465 \times 10^{-4}\,(\cancel{\text{C}}\,\text{s}^{-1}\,\text{V}^{-1})\,\text{cm}^2\,\text{mol}^{-1}\,\cancel{\text{C}^{-1}}$$

$$u_{\text{Cl}^-} = 8.137\,050\,465 \times 10^{-4}\,\text{cm}^2\,\text{mol}^{-1}\,\text{V}^{-1}\,\text{s}^{-1}$$

$$\boxed{u_{\text{Cl}^-} = 8.1 \times 10^{-4}\,\text{cm}^2\,\text{mol}^{-1}\,\text{V}^{-1}\,\text{s}^{-1}}$$

$$u_{\text{Li}^+} = \frac{36.489\,668\,59\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}}{96\,485\,\text{C}}$$

$$u_{\text{Li}^+} = 3.781\,900\,667 \times 10^{-4}\,\text{cm}^2\,\text{mol}^{-1}\,\text{V}^{-1}\,\text{s}^{-1}$$

$$\boxed{u_{\text{Li}^+} = 3.8 \times 10^{-4}\,\text{cm}^2\,\text{mol}^{-1}\,\text{V}^{-1}\,\text{s}^{-1}}$$

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**7.18.** A solution of cadmium iodide,  $\text{CdI}_2$ , having a molality of  $7.545 \times 10^{-3} \text{ mol kg}^{-1}$ , was electrolyzed in a Hittorf cell. The mass of cadmium deposited at the cathode was 0.03462 g. Solution weighing 152.64 g was withdrawn from the anode compartment and was found to contain 0.3718 g of cadmium iodide. Calculate the transport numbers of  $\text{Cd}^{2+}$  and  $\text{I}^-$ .

**Solution:**

Given:  $\text{molality} = 7.545 \times 10^{-3} \text{ mol kg}^{-1}$ ,  $m_{\text{Cd}^{2+}} = 0.03462 \text{ g}$ ,  $m_{\text{anode}} = 152.64 \text{ g}$ ,

$$m_{\text{CdI}_2 \text{ in anode}} = 0.3718 \text{ g}$$

Required:  $t_{\text{Cd}^{2+}}$ ,  $t_{\text{I}^-}$

When working with a Hittorf cell, we must use Eq. 7.75 and Eq. 7.76 to solve for  $t_{\text{Cd}^{2+}}$  and  $t_{\text{I}^-}$ .

$$\frac{\text{amount lost from anode compartment}}{\text{amount deposited}} = t_+ \quad \text{And} \quad \frac{\text{amount lost from cathode compartment}}{\text{amount deposited}} = t_-$$

The number of coulombs of charge will be used as a measure of each amount.

The anode compartment initially contained the following number of moles:

$$n_i = \text{molality} \times m_{\text{anode}}$$

$$n_i = \left( 7.545 \times 10^{-3} \text{ mol } \cancel{\text{kg}^{-1}} \right) \left( 152.64 \cancel{\text{g}} \times 10^{-3} \frac{\cancel{\text{kg}}}{\cancel{\text{g}}} \right)$$

$$n_i = 0.001151669 \text{ mol}$$

The anode compartment finally contained,

$$n_f = \frac{m_{\text{CdI}_2 \text{ in anode}}}{M_{\text{CdI}_2}}$$

$$M_{\text{CdI}_2} = 112.411 \text{ g mol}^{-1} + 2(126.904 47 \text{ g mol}^{-1})$$

$$M_{\text{CdI}_2} = 366.219 94 \text{ g mol}^{-1}$$

$$n_f = \frac{0.3718 \text{ g}}{366.219 94 \text{ g mol}^{-1}}$$

$$n_f = 0.001 015 236 9 \text{ mol}$$

The number of moles lost from the anode compartment is therefore,

$$n = n_i - n_f$$

$$n = 0.001 151 669 \text{ mol} - 0.001 015 236 9 \text{ mol}$$

$$n = 1.364 318 907 \times 10^{-4} \text{ mol}$$

The total amount of  $\text{Cd}^{2+}$  deposited is calculated by,

$$n_{\text{Cd}^{2+}} = \frac{m_{\text{Cd}^{2+}}}{M_{\text{Cd}^{2+}}}$$

$$M_{\text{Cd}^{2+}} = 112.411 \text{ g mol}^{-1}$$

$$n_{\text{Cd}^{2+}} = \frac{0.03462 \text{ g}}{112.411 \text{ g mol}^{-1}}$$

$$n_{\text{Cd}^{2+}} = 3.079 769 773 \times 10^{-4} \text{ mol}$$

Now it is possible to determine the transport number at the anode.

$$t_- = \frac{1.364 318 907 \times 10^{-4} \text{ mol}}{3.079 769 773 \times 10^{-4} \text{ mol}}$$

$$t_- = 0.442 993 797 4$$

$$\boxed{t_- = 0.4430}$$

The second transport number is given by  $1 - t_-$ .

$$t_+ = 1 - 0.442\,993\,797\,4$$

$$t_+ = 0.557\,006\,202\,6$$

$$\boxed{t_+ = 0.5570}$$

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**7.19.** The transport numbers for HCl at infinite dilution are estimated to be  $t^+ = 0.821$  and  $t^- = 0.179$  and the molar conductivity is  $426.16 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Calculate the mobilities of the hydrogen and chloride ions.

**Solution:**

Given:  $t_+ = 0.821$ ,  $t_- = 0.179$ ,  $\Lambda_{\text{HCl}}^\circ = 426.16 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Required:  $u_+$ ,  $u_-$

The ionic mobility is given in terms of molar ionic conductivity by Eq. 7.64.

$$\lambda_+^\circ = \frac{\kappa_+}{c_+} = F u_+$$

The molar ionic conductivities are given by Eq. 7.79.

$$t_+ = \frac{\lambda_+^\circ}{\Lambda^\circ} \text{ and } t_- = \frac{\lambda_-^\circ}{\Lambda^\circ}$$

By rearranging and substituting equations 7.64 and 7.79, we can obtain an expression for the ionic mobility.

$$u = \frac{\lambda^\circ}{F}$$
$$u = \frac{\Lambda^\circ t}{F}$$

Now it is possible to solve for  $u_+$  and  $u_-$ .

$$u_+ = \frac{(426.16 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})(0.821)}{96\,485 \text{ C}}$$

$$u_+ = 0.003\,626\,236 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ C}^{-1}$$

where  $1 \, \Omega^{-1} = 1 \text{ A V}^{-1}$  and  $1 \text{ A} = 1 \text{ C s}^{-1}$

therefore,  $1 \, \Omega^{-1} = 1 \text{ C s}^{-1} \text{ V}^{-1}$

$$u_+ = 0.003\,626\,236 \left( \cancel{\text{C}} \text{ s}^{-1} \text{ V}^{-1} \right) \text{ cm}^2 \text{ mol}^{-1} \cancel{\text{C}^{-1}}$$

$$\boxed{u_+ = 3.63 \times 10^{-3} \text{ V}^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}}$$

$$u_- = \frac{(426.16 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})(0.179)}{96\,485 \text{ C}}$$

$$u_- = 7.906\,165\,725 \times 10^{-4} \text{ V}^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\boxed{u_- = 7.91 \times 10^{-4} \text{ V}^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}}$$

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**7.20.** If a potential gradient of  $100 \text{ V cm}^{-1}$  is applied to a  $0.01 \text{ M}$  solution of  $\text{NaCl}$ , what are the speeds of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions? Take the ionic conductivities to be those listed in Table 7.3 on p. 291.

**Solution:**

Given:  $V = 100 \text{ V cm}^{-1}$ ,  $c_{\text{NaCl}} = 0.01 \text{ M}$ , Table 7.3

Required:  $v_{\text{Na}^+}$ ,  $v_{\text{Cl}^-}$

The ionic mobility is given in terms of the molar ionic conductivity by Eq. 7.64.

$$\lambda_+^\circ = \frac{\kappa_+}{c_+} = F u_+$$

$$u_+ = \frac{\lambda_+^\circ}{F}$$

From Table 7.3 we are given that,

$$\lambda_{\text{Na}^+}^\circ = 50.08 \text{ S cm}^2 \text{ mol}^{-1} \text{ and } \lambda_{\text{Cl}^-}^\circ = 76.31 \text{ S cm}^2 \text{ mol}^{-1}$$

$$u_{\text{Na}^+} = \frac{50.08 \text{ S cm}^2 \cancel{\text{mol}^{-1}}}{96485 \text{ C } \cancel{\text{mol}^{-1}}}$$

$$u_{\text{Na}^+} = 5.19044411 \times 10^{-4} \text{ S cm}^2 \text{ C}^{-1}$$

where  $1 \text{ S} = 1 \Omega^{-1}$  and  $1 \Omega^{-1} = 1 \text{ A V}^{-1}$  and  $1 \text{ A} = 1 \text{ C s}^{-1}$

therefore,  $1 \text{ S} = 1 \text{ C s}^{-1} \text{ V}^{-1}$

$$u_{\text{Na}^+} = 5.19044411 \times 10^{-4} (\cancel{\text{C}} \text{ s}^{-1} \text{ V}^{-1}) \text{ cm}^2 \cancel{\text{C}^{-1}}$$

$$u_{\text{Na}^+} = 5.19044411 \times 10^{-4} \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$$

$$u_{\text{Cl}^-} = \frac{76.31 \text{ S cm}^2 \cancel{\text{mol}^{-1}}}{96485 \text{ C } \cancel{\text{mol}^{-1}}}$$

$$u_{\text{Cl}^-} = 7.909001399 \times 10^{-4} \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$$

From section 7.5 we know that, speed =  $uV$ . The velocities in a gradient of  $100 \text{ V cm}^{-1}$  are thus,

$$v_{\text{Na}^+} = (5.190\,444\,11 \times 10^{-4} \cancel{\text{V}} \text{ cm}^2 \text{ s}^{-1}) (100 \cancel{\text{V}} \cancel{\text{cm}^{-1}})$$

$$v_{\text{Na}^+} = 5.190\,444\,11 \times 10^{-2} \text{ cm s}^{-1}$$

$$\boxed{v_{\text{Na}^+} = 5.19 \times 10^{-2} \text{ cm s}^{-1}}$$

$$v_{\text{Cl}^-} = (7.909\,001\,399 \times 10^{-4} \cancel{\text{V}} \text{ cm}^2 \text{ s}^{-1}) (100 \cancel{\text{V}} \cancel{\text{cm}^{-1}})$$

$$v_{\text{Cl}^-} = 7.909\,001\,399 \times 10^{-2} \text{ cm s}^{-1}$$

$$\boxed{v_{\text{Cl}^-} = 7.91 \times 10^{-2} \text{ cm s}^{-1}}$$

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**7.21.** A solution of LiCl at a concentration of 0.01 M is contained in a tube having a cross-sectional area of  $5 \text{ cm}^2$ . Calculate the speeds of the  $\text{Li}^+$  and  $\text{Cl}^-$  ions if a current of 1 A is passed. Use the ion conductivities listed in Table 7.3.

**Solution:**

Given:  $c_{\text{LiCl}} = 0.01 \text{ M}$ ,  $A = 5 \text{ cm}^2$ ,  $I = 1 \text{ A}$ , Table 7.3

Required:  $v_{\text{Li}^+}$ ,  $v_{\text{Cl}^-}$

In order to determine the speeds of the ions, we must find the potential gradient. Once we have this information, we can proceed in a similar manner as was done in problem 7.20.

The potential gradient can be calculated using Ohm's Law (Eq. 7.7) in conjunction with Eq. 7.9.

$$R = \frac{V}{I} \text{ and } \Lambda = \frac{\kappa}{c}$$

The specific conductivity of a 0.01 M solution is calculated according to:

$$\kappa = c\Lambda$$

We determine the molar conductivity of LiCl using the data for the ionic conductivities of  $\text{Li}^+$  and  $\text{Cl}^-$  found in Table 7.3.

$$\Lambda_{\text{LiCl}}^\circ = \lambda_{\text{Li}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

$$\Lambda_{\text{LiCl}}^\circ = 38.66 \text{ S cm}^2 \text{ mol}^{-1} + 76.31 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\text{LiCl}}^\circ = 114.97 \text{ S cm}^2 \text{ mol}^{-1}$$

Hence,

$$\kappa = (0.01 \times 10^{-3} \text{ mol cm}^{-3}) (114.97 \text{ S cm}^2 \text{ mol}^{-1})$$

$$\kappa = 1.1497 \times 10^{-3} \text{ S cm}^{-1}$$

Let us consider the fact that the resistance is inversely proportional to  $\kappa$ , and we must factor in the  $5 \text{ cm}^2$  of surface area.



$$R = \frac{1}{1.1497 \times 10^{-3} \text{ S cm}^{-1} \times 5 \text{ cm}}$$

$$R = 173.958\,423\,9 \text{ } \Omega \text{ cm}^{-1}$$

The potential gradient required to produce a current of 1 A is therefore,

$$V = (1 \text{ A})(173.958\,423\,9 \text{ } \Omega \text{ cm}^{-1})$$

where  $1 \text{ } \Omega = 1 \text{ V A}^{-1}$

$$V = 173.958\,423\,9 \text{ V cm}^{-1}$$

The ionic mobilities can be calculated using Eq. 7.64.

$$\lambda_+^\circ = \frac{\kappa_+}{c_+} = F u_+$$

$$u_+ = \frac{\lambda_+^\circ}{F}$$

From Table 7.3 we know that,

$$u_{\text{Li}^+} = \frac{38.66 \text{ S cm}^2 \cancel{\text{mol}^{-1}}}{96485 \text{ C } \cancel{\text{mol}^{-1}}}$$

$$u_{\text{Li}^+} = 4.006840442 \times 10^{-4} \text{ S cm}^2 \text{ C}^{-1}$$

where  $1 \text{ S} = 1 \Omega^{-1}$  and  $1 \Omega^{-1} = 1 \text{ A V}^{-1}$  and  $1 \text{ A} = 1 \text{ C s}^{-1}$

therefore,  $1 \text{ S} = 1 \text{ C s}^{-1} \text{ V}^{-1}$

$$\lambda_{\text{Li}^+}^{\circ} = 38.66 \text{ S cm}^2 \text{ mol}^{-1} \text{ and } \lambda_{\text{Cl}^-}^{\circ} = 76.31 \text{ S cm}^2 \text{ mol}^{-1}$$

$$u_{\text{Li}^+} = 4.006840442 \times 10^{-4} (\cancel{\text{C s}^{-1} \text{ V}^{-1}}) \text{ cm}^2 \cancel{\text{C}^{-1}}$$

$$u_{\text{Li}^+} = 4.006840442 \times 10^{-4} \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$$

$$u_{\text{Cl}^-} = \frac{76.31 \text{ S cm}^2 \cancel{\text{mol}^{-1}}}{96485 \text{ C } \cancel{\text{mol}^{-1}}}$$

$$u_{\text{Cl}^-} = 7.909001399 \times 10^{-4} \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$$

From section 7.5 we are given that, speed =  $uV$ .

$$v_{\text{Li}^+} = \left( 4.006840442 \times 10^{-4} \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1} \cancel{\text{V}^{-1} \text{ cm}^2 \text{ s}^{-1}} \right) (173.9584239 \cancel{\text{V}} \cancel{\text{cm}^{-1}})$$

$$v_{\text{Li}^+} = 0.0697023648 \text{ cm s}^{-1}$$

$$\boxed{v_{\text{Li}^+} = 7.0 \times 10^{-2} \text{ cm s}^{-1}}$$

$$v_{\text{Cl}^-} = \left( 7.909001399 \times 10^{-4} \cancel{\text{V}^{-1} \text{ cm}^2 \text{ s}^{-1}} \right) (173.9584239 \cancel{\text{V}} \cancel{\text{cm}^{-1}})$$

$$v_{\text{Cl}^-} = 0.1375837418 \text{ cm s}^{-1}$$

$$\boxed{v_{\text{Cl}^-} = 0.14 \text{ cm s}^{-1}}$$

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**7.22.** What is the work required to separate in vacuum two particles, one with the charge of the proton, from another particle with the same charge of opposite sign? Carry out the calculations for an initial distance of (a) 1.0 nm to an infinite distance apart and (b) from 1.0 mm to an infinite distance apart. (c) In (a) how much work would be required if the charge is moved to a distance of 0.1 m? The charge on a proton is  $1.6 \times 10^{-19}$  C.

**Solution:**

Given: vacuum:  $Q_1 = -Q_2$ ,  $e = 1.6 \times 10^{-19}$  C

Required: see above

Recall that work is defined as the application of a force through a distance. This definition is given by Eq. 1.1,  $dw = \mathbf{F} \cdot d\mathbf{l}$ . In this case, the force we are concerned with is an electrostatic force, and the distance in a vacuum we use as  $r$ .

From Eq. 7.1, the electrostatic force is given by:

$$F = \frac{Q_1 Q_2}{4\pi \epsilon_0 r^2}$$

To determine the amount of work done, we will take the integral of  $F$  with respect to  $r$ .

$$w = \int_{r_1}^{r_2} F dr$$

$$w = \int_{r_1}^{r_2} \frac{Q_1 Q_2}{4\pi \epsilon_0 r^2} dr$$

Since the particles have opposite charges, we will introduce a negative sign.

$$w = \int_{r_1}^{r_2} -\frac{Q_1 Q_2}{4\pi \epsilon_0 r^2} dr$$

$$w = -\frac{Q_1 Q_2}{4\pi \epsilon_0} \left( \frac{1}{r_2} - \frac{1}{r_1} \right)$$

The permittivity of a vacuum has the value,  $\epsilon_0 = 8.854 \times 10^{-12}$  C<sup>2</sup> J<sup>-1</sup> m<sup>-1</sup>. This will be used when solving parts a, b and c.

a)

$$r_1 = 1.0 \times 10^{-9} \text{ m}, r_2 = \infty \text{ m}$$

$$w = - \frac{(1.6 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})} \left( \frac{1}{\infty} - \frac{1}{1.0 \times 10^{-9} \text{ m}} \right)$$

$$w = 2.300\,862\,1 \times 10^{-19} \text{ J}$$

$$\boxed{w = 2.3 \times 10^{-19} \text{ J}}$$

b)

$$r_1 = 1.0 \times 10^{-3} \text{ m}, r_2 = \infty \text{ m}$$

$$w = - \frac{(1.6 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})} \left( \frac{1}{\infty} - \frac{1}{1.0 \times 10^{-3} \text{ m}} \right)$$

$$w = 2.300\,862\,1 \times 10^{-25} \text{ J}$$

$$\boxed{w = 2.3 \times 10^{-25} \text{ J}}$$

c)

$$r_1 = 1.0 \times 10^{-9} \text{ m}, r_2 = 0.10 \text{ m}$$

$$w = - \frac{(1.6 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})} \left( \frac{1}{0.10 \text{ m}} - \frac{1}{1.0 \times 10^{-9} \text{ m}} \right)$$

$$w = 2.300\,862\,1 \times 10^{-19} \text{ J}$$

$$\boxed{w = 2.3 \times 10^{-19} \text{ J}}$$

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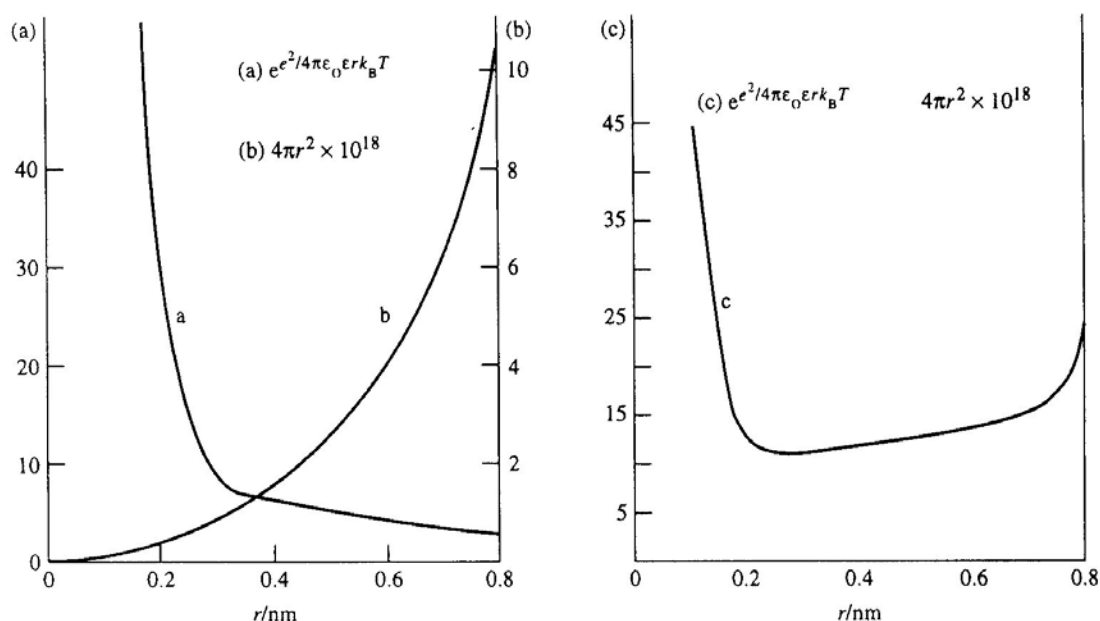
**7.23.** According to Bjerrum's theory of ion association, the number of ions of type  $i$  present in a spherical shell of thickness  $dr$  and distance  $r$  from a central ion is

$$dN_i = N_i \exp(-z_i z_c e^2 / 4\pi \epsilon_0 \epsilon r k_B T) 4\pi r^2 dr$$

where  $z_i$  and  $z_c$  are the charge numbers of the ion of type  $i$  and of the central ion and  $e$ ,  $\epsilon_0$ ,  $\epsilon$ , and  $k_B$  have their usual significance. Plot the exponential in this expression and also  $4\pi r^2$  against  $r$  for a uni-univalent electrolyte in water at 25.0 °C ( $\epsilon = 78.3$ ). Allow  $r$  to have values from 0 to 1 nm. Plot also the product of these functions, which is  $(dN_i/N_i)dr$  and is the probability of finding an ion of type  $i$  at a distance between  $r$  and  $r + dr$  of the central ion.

By differentiation, obtain a value  $r^*$  for which the probability is a minimum, and calculate the value for water at 25.0 °C. The electrostatic potential is given to a good approximation by the first term in Eq. 7.47 on p. 280. Obtain an expression, in terms of  $k_B T$ , for the electrostatic energy between the two univalent ions at this minimum distance, and evaluate this energy at 25 °C.

**Solution:**



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**7.24.** The following are some conventional standard enthalpies of ions in aqueous solution at 25 °C:

Ion	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{H}^+$	0
$\text{Na}^+$	-239.7
$\text{Ca}^{2+}$	-543.1
$\text{Zn}^{2+}$	-152.3
$\text{Cl}^-$	-167.4
$\text{Br}^-$	-120.9

Calculate the enthalpy of formation in aqueous solution of 1 mol of NaCl, CaCl<sub>2</sub>, and ZnBr<sub>2</sub>, assuming complete dissociation.

**Solution:**

Given: standard enthalpies

Required: enthalpies of formation

In order to calculate the enthalpies of formation, we will simply sum up the standard enthalpies of the ions present in the solution.

$$\Delta_f H_{\text{NaCl}} = \Delta_f H_{\text{Na}}^\circ + \Delta_f H_{\text{Cl}}^\circ$$

$$\Delta_f H_{\text{NaCl}} = -239.7 \text{ kJ mol}^{-1} - 167.4 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_f H_{\text{NaCl}} = -407.1 \text{ kJ mol}^{-1}}$$

$$\Delta_f H_{\text{CaCl}_2} = \Delta_f H_{\text{Ca}}^\circ + 2\Delta_f H_{\text{Cl}}^\circ$$

$$\Delta_f H_{\text{CaCl}_2} = -543.1 \text{ kJ mol}^{-1} - 2(167.4 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta_f H_{\text{CaCl}_2} = -877.9 \text{ kJ mol}^{-1}}$$

$$\Delta_f H_{\text{ZnBr}_2} = \Delta_f H_{\text{Zn}}^\circ + 2\Delta_f H_{\text{Br}}^\circ$$

$$\Delta_f H_{\text{ZnBr}_2} = -152.3 \text{ kJ mol}^{-1} - 2(120.9 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta_f H_{\text{ZnBr}_2} = -394.1 \text{ kJ mol}^{-1}}$$

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**7.25.** One estimate for the absolute Gibbs energy of hydration of the  $\text{H}^+$  ion in aqueous solution is  $-1051.4 \text{ kJ mol}^{-1}$ . On this basis, calculate the absolute Gibbs energies of hydration of the following ions, whose conventional standard Gibbs energies of hydration are as follows:

Ion	$\Delta_{\text{hyd}} G^\circ \text{ kJ mol}^{-1}$
$\text{H}^+$	0
$\text{Na}^+$	679.1
$\text{Mg}^{2+}$	274.1
$\text{Al}^{3+}$	-1346.4
$\text{Cl}^-$	-1407.1
$\text{Br}^-$	-1393.3

**Solution:**

Given:  $\Delta_{\text{hyd}} G^\circ_{\text{H}^+} (\text{absolute}) = -1051.4 \text{ kJ mol}^{-1}$

Required:  $\Delta_{\text{hyd}} G^\circ (\text{absolute})$  for each ion

In order to find the absolute Gibbs energies of hydration, we can either lower the cation's standard Gibbs energies of hydration, or raise the anion's absolute Gibbs energies of hydration by  $1051.4 \text{ kJ mol}^{-1}$  (per charge).



$$\Delta_{\text{hyd}} G_{\text{H}^+}^{\circ} (\text{absolute}) = 0 - 1051.4 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{H}^+}^{\circ} (\text{absolute}) = -1051.4 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Na}^+}^{\circ} (\text{absolute}) = 679.1 \text{ kJ mol}^{-1} - 1051.4 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Na}^+}^{\circ} (\text{absolute}) = -372.3 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Mg}^{2+}}^{\circ} (\text{absolute}) = 274.1 \text{ kJ mol}^{-1} - 2(1051.4 \text{ kJ mol}^{-1})$$

$$\Delta_{\text{hyd}} G_{\text{Mg}^{2+}}^{\circ} (\text{absolute}) = -1828.7 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Al}^{3+}}^{\circ} (\text{absolute}) = -1346.4 \text{ kJ mol}^{-1} - 3(1051.4 \text{ kJ mol}^{-1})$$

$$\Delta_{\text{hyd}} G_{\text{Al}^{3+}}^{\circ} (\text{absolute}) = -4500.6 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Cl}^-}^{\circ} (\text{absolute}) = -1407.1 \text{ kJ mol}^{-1} + 1051.4 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Cl}^-}^{\circ} (\text{absolute}) = -355.7 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Br}^-}^{\circ} (\text{absolute}) = -1393.3 \text{ kJ mol}^{-1} + 1051.4 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{hyd}} G_{\text{Br}^-}^{\circ} (\text{absolute}) = -341.9 \text{ kJ mol}^{-1}$$

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**7.26.** Calculate the ionic strengths of 0.1 M solutions of  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{ZnCl}_2$ , and  $\text{K}_4\text{Fe}(\text{CN})_6$ ; assume complete dissociation and neglect hydrolysis.

**Solution:**

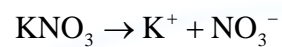
Given:  $c = 0.1 \text{ M}$

Required:  $I$

The ionic strength of a solution is given by Eq. 7.103:

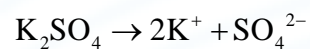
$$I = \frac{1}{2} \sum_i c_i z_i^2$$

where  $z_i$  is the valency of each ion present.



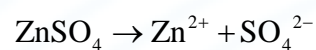
$$I_{\text{KNO}_3} = \frac{1}{2} (0.1 \text{ M} \times 1^2 + 0.1 \text{ M} \times 1^2)$$

$$I_{\text{KNO}_3} = 0.1 \text{ M}$$



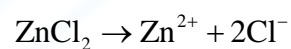
$$I_{\text{K}_2\text{SO}_4} = \frac{1}{2} (0.2 \text{ M} \times 1^2 + 0.1 \text{ M} \times 2^2)$$

$$I_{\text{K}_2\text{SO}_4} = 0.3 \text{ M}$$



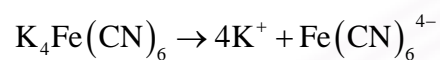
$$I_{\text{ZnSO}_4} = \frac{1}{2} (0.1 \text{ M} \times 2^2 + 0.1 \text{ M} \times 2^2)$$

$$I_{\text{ZnSO}_4} = 0.4 \text{ M}$$



$$I_{\text{ZnCl}_2} = \frac{1}{2} (0.1 \text{ M} \times 2^2 + 0.2 \text{ M} \times 1^2)$$

$$I_{\text{ZnCl}_2} = 0.3 \text{ M}$$



$$I_{\text{K}_4\text{Fe}(\text{CN})_6} = \frac{1}{2} (0.4 \text{ M} \times 1^2 + 0.1 \text{ M} \times 4^2)$$

$$I_{\text{K}_4\text{Fe}(\text{CN})_6} = 1.0 \text{ M}$$

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**7.27.** Calculate the mean activity coefficient  $\gamma_{\pm}$  for the  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions in a saturated solution of  $\text{BaSO}_4$  ( $K_{\text{sp}} = 9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ ) in 0.2 M  $\text{K}_2\text{SO}_4$ , assuming the Debye-Hückel limiting law to apply.

**Solution:**

Given:  $\text{BaSO}_4$ :  $K_{\text{sp}} = 9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ ,  $c_{\text{K}_2\text{SO}_4} = 0.2 \text{ M}$

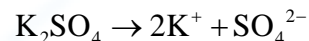
Required:  $\gamma_{\pm}$

When determining the mean activity coefficient, we use the Debye-Hückel limiting law given in Eq. 7.111:

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}$$

We may then calculate the ionic strength from Eq. 7.103 in the following manner,

$$I = \frac{1}{2} \sum_i c_i z_i^2$$



$$I_{\text{K}_2\text{SO}_4} = \frac{1}{2} (0.4 \text{ M} \times 1^2 + 0.2 \text{ M} \times 2^2)$$

$$I_{\text{K}_2\text{SO}_4} = 0.6 \text{ M}$$

Finally we can solve for the mean activity coefficient which produces;

$$\log_{10} \gamma_{\pm} = -0.51 (2 \times 2) \sqrt{0.6}$$

$$\gamma_{\pm} = 10^{-0.51(2 \times 2)\sqrt{0.6}}$$

$$\gamma_{\pm} = 0.0262919498$$

$$\boxed{\gamma_{\pm} = 2.6 \times 10^{-2}}$$

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**7.28.** The solubility of AgCl in water at 25 °C is  $1.274 \times 10^{-5} \text{ mol dm}^{-3}$ . On the assumption that the Debye-Hückel limiting law applies,

a. Calculate  $\Delta G^\circ$  for the process  $\text{AgCl(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ .

b. Calculate the solubility of AgCl in an 0.005 M solution of  $\text{K}_2\text{SO}_4$ .

**Solution:**

Given:  $s = 1.274 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $T = 25^\circ\text{C}$

Required: see above

a. To calculate the Gibbs energy, we first need to determine the solubility product of AgCl in water.

Eq. 7.121 shows that  $K_s = [\text{Ag}^+][\text{Cl}^-]\gamma_\pm^2$ , and since  $[\text{Ag}^+] = [\text{Cl}^-]$ , we can write

$$K_s = s^2 \gamma_\pm^2.$$

We solve for the mean activity coefficient from Eq. 7.111, using the solubility as a measure of ionic strength.

$$\log_{10} \gamma_\pm = -0.51 z_+ |z_-| \sqrt{I/\text{mol dm}^{-3}}$$

$$\log_{10} \gamma_\pm = -0.51(1 \times 1) \sqrt{1.274 \times 10^{-5}}$$

$$\gamma_\pm = 10^{-0.51(1 \times 1) \sqrt{1.274 \times 10^{-5}}}$$

$$\gamma_\pm = 0.9958172614$$

The solubility product is then,

$$K_s = (1.274 \times 10^{-5} \text{ M})^2 (0.9958172614)^2$$

$$K_s = 1.60952659 \times 10^{-10} \text{ M}^2$$

Solving for Gibbs energy, using  $\Delta G^\circ = -RT \ln K_s$ , we obtain

$$\Delta G^\circ = \left( -8.3145 \text{ J } \cancel{\text{K}}^{-1} \text{ mol}^{-1} \right) (298.15 \text{ K}) \ln (1.609\,526\,59 \times 10^{-10} \text{ M}^2)$$

$$\Delta G^\circ = 55\,900.511\,31 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 55.90 \text{ kJ mol}^{-1}}$$

b. To solve for the solubility in a solution of  $c = 0.005 \text{ M}$   $\text{K}_2\text{SO}_4$ , we need to calculate the ionic strength since we have a common ion present.

We can calculate the ionic strength from Eq. 7.103 in the following manner,

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I = \frac{1}{2} (0.01 \text{ M} \times 1^2 + 0.005 \text{ M} \times 2^2)$$

$$I = 0.015 \text{ M}$$

We solve for the mean activity coefficient from Eq. 7.111, using the solubility as a measure of ionic strength.

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}$$

$$\log_{10} \gamma_{\pm} = -0.51 (1 \times 1) \sqrt{0.015}$$

$$\log_{10} \gamma_{\pm} = -0.062\,461\,988$$

$$\gamma_{\pm} = 10^{-0.062\,461\,988}$$

$$\gamma_{\pm} = 0.866\,040\,12$$

Solving for the solubility by rearranging Eq. 7.121,

$$K_s = s^2 \gamma_{\pm}^2$$

$$s = \frac{\sqrt{K_s}}{\gamma_{\pm}}$$

$$s = \frac{\sqrt{1.609\,526\,59 \times 10^{-10} \text{ M}^2}}{0.86604012}$$

$$s = 1.464\,91 \times 10^{-5} \text{ M}$$

$$\boxed{s = 1.46 \times 10^{-5} \text{ M}}$$

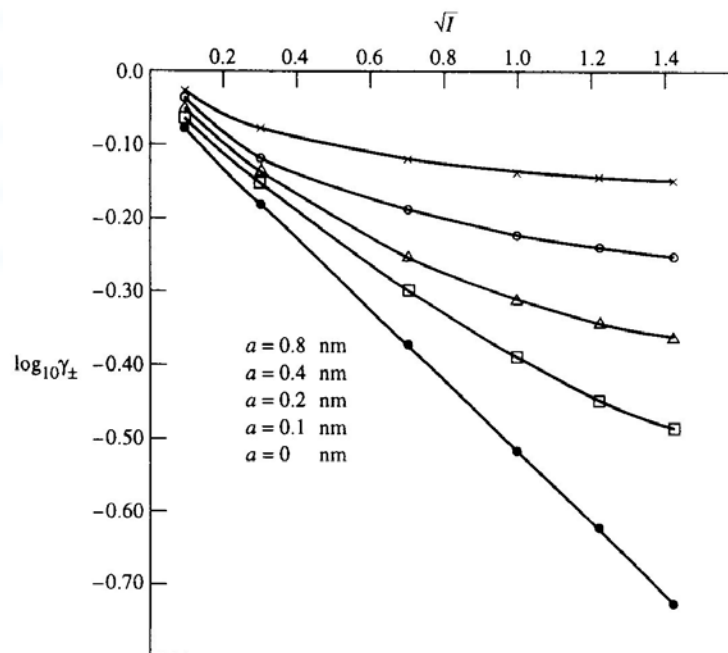
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**7.29.** Employ Eq. 7.114 to make plots of  $\log \gamma_{\pm}$  against  $\sqrt{I}$  for a uni-univalent electrolyte in water at 25 °C, with  $B = 0.51 \text{ mol}^{-1} \text{ dm}^{3/2}$  and  $B' = 0.33 \times 10^{10} \text{ mol}^{-1} \text{ dm}^{3/2} \text{ m}^{-1}$ , and for the following values of the interionic distance  $a$ :

$$a = 0, 0.1, 0.2, 0.4, \text{ and } 0.8 \text{ nm}$$

**Solution:**



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**7.30.** Estimate the change in Gibbs energy  $\Delta G$  when 1 mol of  $K^+$  ions (radius 0.133 nm) is transported from aqueous solution ( $\epsilon = 78$ ) to the lipid environment of a cell membrane ( $\epsilon = 4$ ) at 25 °C.

**Solution:**

Given:  $n = 1$  mol,  $r_{K^+} = 0.133$  nm,  $\epsilon_{\text{water}} = 78$ ,  $\epsilon_{\text{membrane}} = 4$ ,  $T = 25$  °C

Required:  $\Delta G$

Eq. 7.87 (given below) may be used to estimate the change in Gibbs energy.

$$G_{\text{es}}^{\circ} = \frac{z^2 e^2}{8\pi \epsilon_0 \epsilon r}$$

Since we are given 1 mol of  $K^+$ , we will multiply the expression above by  $L$ , Avogadro's number.

$$G_{\text{es}}^{\circ} = \frac{z^2 e^2 L}{8\pi \epsilon_0 \epsilon r}$$

$$G_{\text{es}}^{\circ} = \frac{(+1)^2 (1.602 \times 10^{-19} \text{ C})^2 (6.022 \times 10^{23} \text{ mol}^{-1})}{8\pi (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) (0.133 \times 10^{-9} \text{ m}) \epsilon}$$

$$G_{\text{es}}^{\circ} = \frac{5\,222\,197.4616 \text{ N m mol}^{-1}}{\epsilon}$$

where 1 N m = 1 J

$$G_{\text{es}}^{\circ} = \frac{5\,222\,197.4616 \text{ J mol}^{-1}}{\epsilon}$$

$$G_{\text{water}}^{\circ} = \frac{5\,222\,197.4616 \text{ J mol}^{-1}}{78}$$

$$G_{\text{water}}^{\circ} = 6694.839\,251 \text{ J mol}^{-1}$$

$$G_{\text{membrane}}^{\circ} = \frac{5\,222\,197.4616 \text{ J mol}^{-1}}{4}$$

$$G_{\text{membrane}}^{\circ} = 130\,549.3654 \text{ J mol}^{-1}$$

$$\Delta G_{\text{es}}^{\circ} = G_{\text{membrane}}^{\circ} - G_{\text{water}}^{\circ}$$

$$\Delta G_{\text{es}}^{\circ} = 130\,549.3654 \text{ J mol}^{-1} - 6694.839\,251 \text{ J mol}^{-1}$$

$$\Delta G_{\text{es}}^{\circ} = 123\,854.526\,1 \text{ J mol}^{-1}$$

$$\boxed{\Delta G_{\text{es}}^{\circ} = 124 \text{ kJ mol}^{-1}}$$

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**7.31.** At 18 °C the electrolytic conductivity of a saturated solution of  $\text{CaF}_2$  is  $3.86 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ , and that of pure water is  $1.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ . The molar ionic conductivities of  $\frac{1}{2}\text{Ca}^{2+}$  and  $\text{F}^-$  are  $51.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and  $47.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively. Calculate the solubility of  $\text{CaF}_2$  in pure water at 18 °C and the solubility product.

**Solution:**

Given:  $T = 18^\circ\text{C}$ ,  $\kappa_{\text{CaF}_2} = 3.86 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ ,  $\kappa_{\text{H}_2\text{O}} = 1.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ ,

$$\lambda_{\frac{1}{2}\text{Ca}^{2+}} = 51.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, \lambda_{\text{F}^-} = 47.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Required:  $s$ ,  $K_s$

The expression for the molar conductivity is given by Eq. 7.9:

$$\Lambda = \frac{\kappa}{c}$$

It is possible to use the concentration to determine the solubility.

$$c = \frac{\kappa}{\Lambda_{\frac{1}{2}\text{CaF}_2}}$$

$$\Lambda_{\frac{1}{2}\text{CaF}_2} = \lambda_{\frac{1}{2}\text{Ca}^{2+}} + \lambda_{\text{F}^-}$$

$$\Lambda_{\frac{1}{2}\text{CaF}_2} = 51.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} + 47.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\frac{1}{2}\text{CaF}_2} = 98.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

The observed  $\kappa$  due to the salt is therefore,

$$\kappa = 3.86 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1} - 1.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$$

$$\kappa = 3.71 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$$

$$c = \frac{3.71 \times 10^{-5} \cancel{\Omega^{-1}} \text{ cm}^{-1}}{98.1 \cancel{\Omega^{-1}} \text{ cm}^2 \text{ mol}^{-1}}$$

$$c = 3.78185525 \times 10^{-7} \text{ mol cm}^{-3}$$

$$c = 3.78185525 \times 10^{-4} \text{ mol dm}^{-3}$$

$\frac{1}{2}\text{CaF}_2$  has the molar mass,

$$M_{\frac{1}{2}\text{CaF}_2} = \frac{1}{2}(40.078 \text{ g mol}^{-1}) + 18.9984032 \text{ g mol}^{-1}$$

$$M_{\text{CaF}_2} = 39.0374032 \text{ g mol}^{-1}$$

The solubility can now be determined.

$$s = (39.0374032 \text{ g } \cancel{\text{mol}^{-1}})(3.78185525 \times 10^{-4} \cancel{\text{mol dm}^{-3}})$$

$$s = 0.0147633808 \text{ g dm}^{-3}$$

$$\boxed{s = 1.48 \times 10^{-2} \text{ g dm}^{-3}}$$

The solubility product is given by,

$$K_s = [\text{Ca}^{2+}][\text{F}^-]^2$$

$$K_s = \left(\frac{1}{2}(3.78185525 \times 10^{-4} \text{ mol dm}^{-3})\right)(3.78185525 \times 10^{-4} \text{ mol dm}^{-3})^2$$

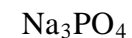
$$K_s = 2.70448584 \times 10^{-11} \text{ mol dm}^{-3}$$

$$\boxed{K_s = 2.70 \times 10^{-11} \text{ mol dm}^{-3}}$$

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**7.32.** What concentrations of the following have the same ionic strength as 0.1 M NaCl?



Assume complete dissociation and neglect hydrolysis.

**Solution:**

Given:  $c_{\text{NaCl}} = 0.1 \text{ M}$

Required:  $c_{\text{CuSO}_4}, c_{\text{Ni}(\text{NO}_3)_2}, c_{\text{Al}_2(\text{SO}_4)_3}, c_{\text{Na}_3\text{PO}_4}$

As we have previously seen, the ionic strength of a compound may be determined using Eq. 7.103.

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I_{\text{NaCl}} = \frac{1}{2} (0.1 \text{ M} \times 1^2 + 0.1 \text{ M} \times 1^2)$$

$$I_{\text{NaCl}} = 0.1 \text{ M}$$

For each salt, we set  $I = I_{\text{NaCl}} = 0.1 \text{ M}$  to solve for  $c$ .

$$0.1 \text{ M} = \frac{1}{2} (c_{\text{CuSO}_4} \times 2^2 + c_{\text{CuSO}_4} \times 2^2)$$

$$0.1 \text{ M} = 4c_{\text{CuSO}_4}$$

$$c_{\text{CuSO}_4} = 2.5 \times 10^{-2} \text{ M}$$

$$0.1 \text{ M} = \frac{1}{2} (c_{\text{Ni(NO}_3)_2} \times 2^2 + 2c_{\text{Ni(NO}_3)_2} \times 1^2)$$

$$0.1 \text{ M} = 3c_{\text{Ni(NO}_3)_2}$$

$$c_{\text{Ni(NO}_3)_2} = 3.3 \times 10^{-2} \text{ M}$$

$$0.1 \text{ M} = \frac{1}{2} (2c_{\text{Al}_2(\text{SO}_4)_3} \times 3^2 + 3c_{\text{Al}_2(\text{SO}_4)_3} \times 2^2)$$

$$0.1 \text{ M} = 15c_{\text{Al}_2(\text{SO}_4)_3}$$

$$c_{\text{Al}_2(\text{SO}_4)_3} = 6.7 \times 10^{-3} \text{ M}$$

$$0.1 \text{ M} = \frac{1}{2} (3c_{\text{Na}_3\text{PO}_4} \times 1^2 + c_{\text{Na}_3\text{PO}_4} \times 3^2)$$

$$0.1 \text{ M} = 6c_{\text{Na}_3\text{PO}_4}$$

$$c_{\text{Na}_3\text{PO}_4} = 1.7 \times 10^{-2} \text{ M}$$

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**7.33.** The solubility product of  $\text{PbF}_2$  at  $25.0\text{ }^\circ\text{C}$  is  $4.0 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ . Assuming the Debye-Hückel limiting law to apply, calculate the solubility of  $\text{PbF}_2$  in (a) pure water and (b)  $0.01 \text{ M NaF}$ .

**Solution:**

Given:  $K_s = 4.0 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ ,  $T = 25\text{ }^\circ\text{C}$

Required: see above

**a)** The dissolution of  $\text{PbF}_2$  is written as:  $\text{PbF}_2 \rightarrow \text{Pb}^{2+} + 2\text{F}^-$ , hence the solubility product is given by:

$$K_s = [\text{Pb}^{2+}][\text{F}^-]^2.$$

In order to solve for solubility, we must first neglect the effect of the activity coefficients and write,  $K_s = [s][2s]^2 = 4s^3$ .

Solving for  $s$ , we obtain,

$$4s^3 = 4.0 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$$

$$s = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$$

We will determine the activity coefficients of  $\text{Pb}^{2+}$  and  $\text{F}^-$  by applying the Debye-Hückel limiting law. To solve, we must first calculate the ionic strength of  $\text{PbF}_2$  from Eq. 7.103.

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I = \frac{1}{2} (s \times 2^2 + 2s \times 1^2)$$

$$I = 3s$$

$$I = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$$

According to the Debye-Hückel limiting law, Eq. 7.111,

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I/\text{mol dm}^{-3}}$$

$$\gamma_{\pm} = 10^{-0.51 z_+ |z_-| \sqrt{I/\text{mol dm}^{-3}}}$$

$$\gamma_{\pm} = 10^{-0.51(2 \times 1) \sqrt{3.0 \times 10^{-3}}}$$

$$\gamma_{\pm} = 0.879\,290\,334\,3$$

In order to find the true solubility, we must factor in the activity coefficients.

$$K_s = [\gamma_+ s][2\gamma_- s]^2 = 4s^3$$

$$s^3 = \frac{K_s}{4\gamma_+ \gamma_-^2}$$

$$s = \sqrt[3]{\frac{4.0 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}}{4(0.879\,290\,334\,3)^3}}$$

$$s = 1.137\,280\,8 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\boxed{s = 1.1 \times 10^{-3} \text{ mol dm}^{-3}}$$

**b)** In 0.01 M NaF, the ionic strength is essentially  $0.01 \text{ mol dm}^{-3}$ . Calculating the activity coefficients, we obtain,

$$\gamma_{\pm} = 10^{-0.51 z_+ |z_-| \sqrt{I/\text{mol dm}^{-3}}}$$

$$\gamma_{\pm} = 10^{-0.51(2 \times 1) \sqrt{0.01}}$$

$$\gamma_{\pm} = 0.790\,678\,628$$

If  $s$  is the solubility then,



$$K_s = [\text{Pb}^{2+}][\text{F}^-]^2$$

$$[\text{Pb}^{2+}] = s$$

$$[\text{F}^-] = 0.01 \text{ mol dm}^{-3}$$

$$K_s = [\gamma_+ s][\gamma_- 0.01 \text{ mol dm}^{-3}]^2$$

$$K_s = (\gamma_+ \gamma_-^2 0.0001 \text{ mol}^2 \text{ dm}^{-6}) s$$

$$s = \frac{K_s}{(\gamma_+ \gamma_-^2 0.0001 \text{ mol}^2 \text{ dm}^{-6})}$$

$$s = \frac{4.0 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}}{(0.790\,678\,628)^3 0.0001 \text{ mol}^2 \text{ dm}^{-6}}$$

$$s = 8.092\,076\,715 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\boxed{s = 8.1 \times 10^{-5} \text{ mol dm}^{-3}}$$

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**7.34.** Calculate the solubility of silver acetate in water at 25 °C, assuming the DHLL to apply; the solubility product is  $4.0 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}$ .

**Solution:**

Given:  $K_s = 4.0 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}$ ,  $T = 25 \text{ °C}$

Required:  $s$

We will solve this problem in a similar manner as the previous question. We may start by neglecting the activity coefficients to find the first approximation of  $s$ .

The dissolution of silver acetate is given by the following:



$$K_s = [s][s] = s^2$$

$$s = \sqrt{K_s}$$

$$s = \sqrt{4.0 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}}$$

$$s = 0.063\,245\,553\,2 \text{ mol dm}^{-3}$$

The ionic strength is thus,

$$I = \frac{1}{2} (s \times 1^2 + s \times 1^2)$$

$$I = s = 0.063\,245\,553\,2 \text{ mol dm}^{-3}$$

According to the Debye-Hückel limiting law, Eq. 7.111,

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}$$

$$\gamma_{\pm} = 10^{-0.51(1 \times 1) \sqrt{0.063\,245\,553\,2}}$$

$$\gamma_{\pm} = 0.744\,289\,325$$

The second approximation of the solubility is therefore,

$$K_s = [\gamma_+ s][\gamma_- s] = \gamma_+ \gamma_- s^2$$

$$s = \sqrt{\frac{K_s}{\gamma_+ \gamma_-}}$$

$$s = \sqrt{\frac{4.0 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}}{(0.744\,289\,325)^2}}$$

$$s = 0.084\,974\,419\,3 \text{ mol dm}^{-3}$$

$$\boxed{s = 8.5 \times 10^{-2} \text{ mol dm}^{-3}}$$

We may continue to take third and fourth approximations by repeating the above steps.

$$\gamma_{\pm} = 10^{-0.51(1 \times 1)\sqrt{0.084\,974\,419\,3}}$$

$$\gamma_{\pm} = 0.710\,122\,220\,4$$

$$s = \sqrt{\frac{K_s}{\gamma_+ \gamma_-}}$$

$$s = \sqrt{\frac{4.0 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}}{(0.710\,122\,220\,4)^2}}$$

$$s = 0.089\,062\,912\,5 \text{ mol dm}^{-3}$$

The third approximation is then;  $\boxed{s = 8.9 \times 10^{-2} \text{ mol dm}^{-3}}$ .

$$\gamma_{\pm} = 10^{-0.51(1 \times 1)\sqrt{0.089\,062\,912\,5}}$$

$$\gamma_{\pm} = 0.704\,366\,363\,8$$

$$s = \sqrt{\frac{K_s}{\gamma_+ \gamma_-}}$$

$$s = \sqrt{\frac{4.0 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}}{(0.704\,366\,363\,8)^2}}$$

$$s = 0.089\,790\,706\,2 \text{ mol dm}^{-3}$$

The fourth approximation is then;  $s = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ .

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**7.35.** Problem 7.30 was concerned with the Gibbs energy change when 1 mol of  $K^+$  ions are transported from water to a lipid. Estimate the electrostatic contribution to the entropy change when this occurs, assuming the dielectric constant of the lipid to be temperature independent, and the following values for water at 25 °C:  $\epsilon = 78$ ;  $\partial \ln \epsilon / \partial T = -0.0046 \text{ K}^{-1}$ . Suggest a qualitative explanation for the sign of the value you obtain.

**Solution:**

Given: Problem 7.30:  $T = 25 \text{ °C}$ ,  $\epsilon = 78$ ,  $\frac{\partial \ln \epsilon}{\partial T} = -0.0046$

Required:  $\Delta S_{\text{es}}^\circ$ , explain the sign

From Problem 7.30, we found the expression for the estimated Gibbs energy,

$$G_{\text{es}}^\circ = \frac{5\,222\,197.4616 \text{ J mol}^{-1}}{\epsilon}$$

For the transfer from water to lipid we can say that,

$$\Delta G_{\text{es}}^\circ / \text{J mol}^{-1} = 5\,222\,197.4616 \left( \frac{1}{\epsilon_{\text{lipid}}} - \frac{1}{\epsilon_{\text{water}}} \right)$$

From Eq. 3.119:

$$\left( \frac{\partial G}{\partial T} \right)_P = -S$$

$$\text{hence, } \Delta S_{\text{es}}^\circ = - \left( \frac{\partial G_{\text{es}}^\circ}{\partial T} \right)_P$$

$$\Delta S_{\text{es}}^\circ / \text{J K}^{-1} \text{ mol}^{-1} = -5\,222\,197.4616 \frac{\partial}{\partial T} \left( \frac{1}{\epsilon_{\text{lipid}}} - \frac{1}{\epsilon_{\text{water}}} \right)$$

Since  $\epsilon_{\text{lipid}}$  is temperature independent, this leads to:

$$\Delta S_{\text{es}}^{\circ} / \text{J K}^{-1} \text{ mol}^{-1} = -5\,222\,197.4616 \frac{\partial}{\partial T} \left( -\frac{1}{\epsilon_{\text{water}}} \right)$$

$$\Delta S_{\text{es}}^{\circ} / \text{J K}^{-1} \text{ mol}^{-1} = -5\,222\,197.4616 \frac{1}{\epsilon_{\text{water}}^2} \frac{\partial \epsilon}{\partial T}$$

$$\text{since } \frac{1}{\epsilon_{\text{water}}^2} \frac{\partial \epsilon}{\partial T} = \frac{1}{\epsilon_{\text{water}}} \frac{\partial \ln \epsilon}{\partial T}$$

$$\Delta S_{\text{es}}^{\circ} / \text{J K}^{-1} \text{ mol}^{-1} = -5\,222\,197.4616 \frac{1}{\epsilon_{\text{water}}} \frac{\partial \ln \epsilon}{\partial T}$$

$$\Delta S_{\text{es}}^{\circ} / \text{J K}^{-1} \text{ mol}^{-1} = -5\,222\,197.4616 \left( \frac{1}{78} \right) (-0.0046)$$

$$\Delta S_{\text{es}}^{\circ} = 30.796\,260\,56 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta S_{\text{es}}^{\circ} = 31 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The entropy increases due to the release of bound water molecules when the  $\text{K}^{+}$  ions pass into the lipid.

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**7.36.** Assuming the Born equation (Eq. 7.86) to apply, make an estimate of the reversible work of charging 1 mol of  $\text{Na}^+\text{Cl}^-$  in aqueous solution at 25 °C ( $\epsilon = 78$ ), under the following conditions:

- The electrolyte is present at infinite dilution.
- The electrolyte is present at such a concentration that the mean activity coefficient is 0.70.

The ionic radii are 95 pm for  $\text{Na}^+$  and 181 pm for  $\text{Cl}^-$ .

**Solution:**

Given: Eq. 7.86,  $n = 1$  mol,  $T = 25$  °C,  $\epsilon = 78$

Required: see above

**a)** At infinite dilution, the work of charging an ion is given by Eq. 7.86 which states,

$$w_{\text{rev}} = \frac{z^2 e^2}{8\pi \epsilon_0 \epsilon r}$$

For one mole of  $\text{Na}^+$ , we multiply by Avogadro's number,  $L$  and use the ionic radius of  $r = 95$  pm.

$$w_{\text{Na}^+} = \frac{z^2 e^2 L}{8\pi \epsilon_0 \epsilon r}$$

$$w_{\text{Na}^+} = \frac{(+1)^2 (1.602 \times 10^{-19} \text{ C})^2 (6.022 \times 10^{23} \text{ mol}^{-1})}{8\pi (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) (78) (95 \times 10^{-12} \text{ m})}$$

$$w_{\text{Na}^+} = 9372.774 \text{ 952 N m mol}^{-1}$$

$$w_{\text{Na}^+} = 9372.774 \text{ 952 J mol}^{-1}$$

For one mole of  $\text{Cl}^-$ , we will multiply by Avogadro's number,  $L$  and use the ionic radius of  $r = 181$  pm.

$$w_{\text{Cl}^-} = \frac{(-1)^2 (1.602 \times 10^{-19} \text{ C})^2 (6.022 \times 10^{23} \text{ mol}^{-1})}{8\pi (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) (78) (181 \times 10^{-12} \text{ m})}$$

$$w_{\text{Cl}^-} = 4919.412\,267 \text{ J mol}^{-1}$$

One mole of  $\text{Na}^+\text{Cl}^-$  at infinite dilution is thus,

$$w_{\text{rev}} = w_{\text{Na}^+} + w_{\text{Cl}^-}$$

$$w_{\text{rev}} = 9372.774\,952 \text{ J mol}^{-1} + 4919.412\,267 \text{ J mol}^{-1}$$

$$w_{\text{rev}} = 14\,292.187\,22 \text{ J mol}^{-1}$$

$$\boxed{w_{\text{rev}} = 14 \text{ kJ mol}^{-1}}$$

**b)** These values are reduced when the electrolyte is at a higher concentration. The work of charging the ionic atmosphere is negative and equal to  $kT \ln \gamma_i$ . Thus for one mol of  $\text{Na}^+$  ions, of activity  $\gamma_+$ , the work of charging the atmosphere is  $RT \ln \gamma_+$ . Similarly, for the chloride ion, the work per mole is  $RT \ln \gamma_-$ .

For one mole of  $\text{Na}^+\text{Cl}^-$

$$w_{\text{rev}} = RT (\ln \gamma_+ + \ln \gamma_-)$$

$$w_{\text{rev}} = RT \ln (\gamma_+ \gamma_-)$$

$$w_{\text{rev}} = 2RT \ln \gamma_{\pm}$$

$$\text{where } \gamma_{\pm} = 0.70$$

$$w_{\text{rev}} = 2 (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K}) \ln 0.70$$

$$w_{\text{rev}} = -1768.371\,67 \text{ J mol}^{-1}$$

The net work done is given by,

$$w_{\text{rev}} = 14\,292.187\,22 \text{ J mol}^{-1} - 1768.371\,67 \text{ J mol}^{-1}$$

$$w_{\text{rev}} = 12\,523.815\,55 \text{ J mol}^{-1}$$

$$\boxed{w_{\text{rev}} = 13 \text{ kJ mol}^{-1}}$$



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**7.37.** If the solubility product of barium sulfate is  $9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ , calculate the solubility of  $\text{BaSO}_4$  in a solution that is 0.10 M in  $\text{NaNO}_3$  and 0.20 M in  $\text{Zn}(\text{NO}_3)_2$ ; assume the DHLL to apply.

**Solution:**

Given:  $K_s = 9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ ,  $c_{\text{in NaNO}_3} = 0.10 \text{ M}$ ,  $c_{\text{in Zn}(\text{NO}_3)_2} = 0.20 \text{ M}$

Required:  $s$

The expression for the solubility product is given by,

$$K_s = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$K_s = [\gamma_+ s][\gamma_- s]$$

$$K_s = \gamma_{\pm}^2 s^2$$

The ionic strength of the solution is calculated according to Eq. 7.103.

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I = \frac{1}{2} (1^2 \times 0.1 \text{ M} + 1^2 \times 0.1 \text{ M} + 2^2 \times 0.2 \text{ M} + 1^2 \times 0.4 \text{ M})$$

$$I = 0.70 \text{ M}$$

To find the activity coefficient, we will use the Debye-Hückel limiting law given by Eq. 7.111.

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}$$

$$\gamma_{\pm} = 10^{-0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}}$$

$$\gamma_{\pm} = 10^{-0.51(2 \times 2) \sqrt{0.70}}$$

$$\gamma_{\pm} = 0.019\,643\,259\,1$$

If the solubility  $s$  is therefore,

$$s = \sqrt{\frac{K_s}{\gamma_{\pm}^2}}$$

$$s = \sqrt{\frac{9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}}{(0.019\,643\,259\,1)^2}}$$

$$s = 4.882\,928\,531 \times 10^{-4} \text{ M}$$

$$\boxed{s = 4.9 \times 10^{-4} \text{ M}}$$

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**7.38.** Silver chloride, AgCl, is found to have a solubility of  $1.561 \times 10^{-5}$  M in a solution that is 0.01 M in  $K_2SO_4$ . Assume the DHLL to apply and calculate the solubility in pure water.

**Solution:**

Given:  $s = 1.561 \times 10^{-5}$  M,  $c = 0.01$  M

Required:  $s$

The expression for the solubility product is given by,

$$K_s = [Ag^+][Cl^-]$$

$$K_s = [\gamma_+ s][\gamma_- s]$$

$$K_s = \gamma_{\pm}^2 s^2$$

The ionic strength of the solution is calculated according to Eq. 7.103.

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I = \frac{1}{2} (1^2 \times 0.02 \text{ M} + 2^2 \times 0.01 \text{ M})$$

$$I = 0.03 \text{ M}$$

To determine the activity coefficient, we will use the Debye-Hückel limiting law, Eq. 7.111.

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}$$

$$\gamma_{\pm} = 10^{-0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}}$$

$$\gamma_{\pm} = 10^{-0.51(1 \times 1) \sqrt{0.03}}$$

$$\gamma_{\pm} = 0.8159534984$$

If the solubility product is  $K_s$ ,

$$K_s = (0.815\,953\,498\,4)^2 (1.561 \times 10^{-5} \text{ M})^2$$

$$K_s = 1.622\,320\,38 \times 10^{-10} \text{ M}^2$$

Finally, the solubility in pure water is given by;

$$s = \sqrt{K_s}$$

$$s = \sqrt{1.622\,320\,38 \times 10^{-10} \text{ M}^2}$$

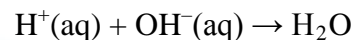
$$s = 1.273\,703\,411 \times 10^{-5} \text{ M}$$

$$\boxed{s = 1.3 \times 10^{-5} \text{ M}}$$

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**7.39.** The enthalpy of neutralization of a strong acid by a strong base, corresponding to the process



is  $-55.90 \text{ kJ mol}^{-1}$ . The enthalpy of neutralization of HCN by NaOH is  $-12.13 \text{ kJ mol}^{-1}$ . Make an estimate of the enthalpy of dissociation of HCN.

**Solution:**

Given:  $\Delta H = -55.90 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{neut}} H = -12.13 \text{ kJ mol}^{-1}$

Required:  $\Delta_{\text{diss}} H$

The enthalpy change for the neutralization of HCN by NaOH is less than the value of the  $55.90 \text{ kJ mol}^{-1}$  because the energy required for the dissociation of HCN,  $\Delta_{\text{diss}} H$  is given by:

$$\Delta_{\text{neut}} H = \Delta H - \Delta_{\text{diss}} H, \text{ hence,}$$

$$\Delta_{\text{diss}} H = \Delta H - \Delta_{\text{neut}} H$$

$$\Delta_{\text{diss}} H = 55.90 \text{ kJ mol}^{-1} - 12.13 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_{\text{diss}} H = 43.77 \text{ kJ mol}^{-1}}$$

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**7.40.** Make use of the Debye-Hückel limiting law to estimate the activity coefficients of the ions in an aqueous 0.004 M solution of sodium sulfate at 298 K. Estimate also the mean activity coefficient.

**Solution:**

Given:  $c_{\text{Na}_2\text{SO}_4} = 0.004 \text{ M}$ ,  $T = 298 \text{ K}$

Required:  $\gamma_{\text{Na}^+}$ ,  $\gamma_{\text{SO}_4^{2-}}$ ,  $\gamma_{\pm}$

From Eq. 7.104 we can calculate the activity coefficients for each ion.

$$\log_{10} \gamma_i = -z_i^2 B \sqrt{I}$$

As we know, the ionic strength of the solution is calculated using Eq. 7.103.

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I = \frac{1}{2} (1^2 \times 0.008 \text{ M} + 2^2 \times 0.004 \text{ M})$$

$$I = 0.012 \text{ M}$$

The activity coefficients are therefore,

$$\gamma_{\text{Na}^+} = 10^{-(+1)^2 0.51 \sqrt{0.012}}$$

$$\gamma_{\text{Na}^+} = 0.879 \, 290 \, 334 \, 3$$

$$\boxed{\gamma_{\text{Na}^+} = 0.879}$$

$$\gamma_{\text{SO}_4^{2-}} = 10^{-(-2)^2 0.51 \sqrt{0.012}}$$

$$\gamma_{\text{SO}_4^{2-}} = 0.597 \, 763 \, 229 \, 5$$

$$\boxed{\gamma_{\text{SO}_4^{2-}} = 0.598}$$

The mean activity coefficient can be determined by using Eq. 7.111 which produces,

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I/\text{mol dm}^{-3}}$$

$$\gamma_{\pm} = 10^{-0.51 z_+ |z_-| \sqrt{I/\text{mol dm}^{-3}}}$$

$$\gamma_{\pm} = 10^{-0.51(1 \times 2)\sqrt{0.012}}$$

$$\gamma_{\pm} = 0.7731514919$$

$$\boxed{\gamma_{\pm} = 0.773}$$

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**7.41.** A 0.1 M solution of sodium palmitate,  $\text{C}_{15}\text{H}_{31}\text{COONa}$ , is separated from a 0.2 M solution of sodium chloride by a membrane that is permeable to  $\text{Na}^+$  and  $\text{Cl}^-$  ions but not to palmitate ions. Calculate the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  ions on the two sides of the membrane after equilibrium has become established. (For a calculation of the Nernst potential, see Problem 8.18.)

**Solution:**

Given:  $c_{\text{NaP}} = 0.1 \text{ M}$ ,  $c_{\text{NaCl}} = 0.2 \text{ M}$

Required:  $c_{\text{Na}^+}$ ,  $c_{\text{Cl}^-}$  on each side of the membrane at equilibrium

	Palmitate Side	Other Side
Initial concentrations	$[\text{Na}^+] = 0.1 \text{ M}$ $[\text{P}^-] = 0.1 \text{ M}$	$[\text{Na}^+] = 0.2 \text{ M}$ $[\text{Cl}^-] = 0.2 \text{ M}$
Final concentrations	$[\text{Na}^+] = (0.1 \text{ M} + x)$ $[\text{P}^-] = 0.1 \text{ M}$ $[\text{Cl}^-] = x$	$[\text{Na}^+] = (0.2 \text{ M} - x)$ $[\text{Cl}^-] = (0.2 \text{ M} - x)$

At equilibrium, the final concentration of NaCl on each side of the membrane will be the same. This allows us to solve for  $x$ .

$$(0.2 \text{ M} - x)^2 = (0.1 + x)x$$

$$0.04 - 0.4x + \cancel{x^2} = 0.1x + \cancel{x^2}$$

$$0.04 = 0.5x$$

$$x = 0.08$$

The final concentrations are thus,

	Palmitate Side	Other Side
Final concentrations	$[\text{Na}^+] = (0.1 \text{ M} + 0.08 \text{ M})$	$[\text{Na}^+] = [\text{Cl}^-] = (0.2 \text{ M} - x)$
	$[\text{Na}^+] = 0.18 \text{ M}$	$[\text{Na}^+] = [\text{Cl}^-] = (0.2 \text{ M} - 0.08 \text{ M})$
	$[\text{Cl}^-] = 0.08 \text{ M}$	$[\text{Na}^+] = [\text{Cl}^-] = 0.12 \text{ M}$

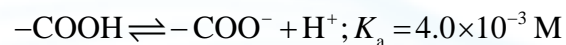
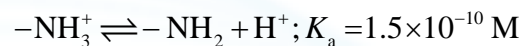
[Back to Problem 7.41](#)

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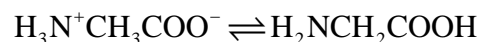
**7.42.** Consider the ionizations



Assume that the following acid dissociation constants apply to the ionizations:



Estimate a value for the equilibrium constant for the process



**Solution:**

Given:  $K_{-\text{NH}_3^+} = 1.5 \times 10^{-10} \text{ M}$ ,  $K_{-\text{COOH}} = 4.0 \times 10^{-3} \text{ M}$

Required:  $K_{\text{NH}_3^+\text{CH}_3\text{COO}^-}$

The equilibrium constant  $K_{-\text{NH}_3^+}$  is given by,

$$K_{-\text{NH}_3^+} = \frac{[\text{H}_2\text{NCH}_2\text{COOH}][\text{H}^+]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COOH}]}$$

And  $K_{-\text{COOH}}$  is given by,

$$K_{-\text{COOH}} = \frac{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COOH}]}$$

We can rearrange the two expressions to obtain an expression for  $K_{\text{NH}_3^+\text{CH}_3\text{COO}^-}$ , and solve for its value.

$$K_{\text{NH}_3^+\text{CH}_3\text{COO}} = \frac{K_{-\text{NH}_3^+}}{K_{-\text{COOH}}}$$

$$K_{\text{NH}_3^+\text{CH}_3\text{COO}} = \frac{[\text{H}_2\text{NCH}_2\text{COOH}]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]}$$

$$K_{\text{NH}_3^+\text{CH}_3\text{COO}} = \frac{1.5 \times 10^{-10} \cancel{\text{M}}}{4.0 \times 10^{-3} \cancel{\text{M}}}$$

$$K_{\text{NH}_3^+\text{CH}_3\text{COO}} = 3.75 \times 10^{-8}$$

$$\boxed{K_{\text{NH}_3^+\text{CH}_3\text{COO}} = 3.8 \times 10^{-8}}$$

[Back to Problem 7.42](#)

[Back to Top](#)

**7.43.** The  $pK$  values for the successive ionizations of phosphoric acid are given on p. 308. Which of the four species is predominant at the following values of the hydrogen or hydroxide concentration?

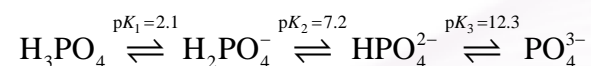
- a.  $[H^+] = 0.1 \text{ M}$ .
- b.  $[H^+] = 2 \times 10^{-3} \text{ M}$ .
- c.  $[H^+] = 5 \times 10^{-5} \text{ M}$ .
- d.  $[OH^-] = 2 \times 10^{-3} \text{ M}$ .
- e.  $[OH^-] = 1 \text{ M}$ .

**Solution:**

Given: p. 308

Required: see above

The successive ionizations of phosphoric acid are given by the following expression.



In order to determine the pH we will use,  $pH = -\log_{10}[H^+]$  and  $pH = 14 - pOH$ .

- a.  $pH = -\log_{10}(0.1)$   $H_3PO_4$  is predominant  
 $pH = 1$
- b.  $pH = -\log_{10}(2 \times 10^{-3})$   $HPO_4^{2-}$  is predominant  
 $pH = 2.698$
- c.  $pH = -\log_{10}(5 \times 10^{-5})$   $HPO_4^{2-}$  is predominant  
 $pH = 4.301$
- d.  $pOH = -\log_{10}(2 \times 10^{-3})$   $HPO_4^{2-}$  is predominant  
 $pOH = 2.698$   
 $pH = 14 - 2.698$   
 $pH = 11.304$

- e.  $\text{pOH} = -\log_{10} 1$   $\text{PO}_4^{3-}$  is predominant  
 $\text{pOH} = 0$   
 $\text{pH} = 14$

[Back to Problem 7.43](#)

[Back to Top](#)

**7.44.** Two solutions of equal volume are separated by a membrane which is permeable to  $K^+$  and  $Cl^-$  ions but not to  $P^-$  ions. The initial concentrations are as shown below.

$$[K^+] = 0.05 \text{ M}$$

$$[Cl^-] = 0.05 \text{ M}$$

$$[K^+] = 0.15 \text{ M}$$

$$[P^-] = 0.15 \text{ M}$$

Calculate the concentrations on each side of the membrane after equilibrium has become established. (See Problem 8.26 in Chapter 8 for the calculation of the Nernst potential for this system.)

**Solution:**

Given: see above

Required:  $c_{K^+}, c_{Cl^-}$  on each side of the membrane at equilibrium

We can solve this problem in a similar manner as problem 7.41.

	Left-hand Side	Right-hand Side
Initial concentrations	$[K^+] = 0.05 \text{ M}$	$[K^+] = 0.15 \text{ M}$
	$[Cl^-] = 0.05 \text{ M}$	$[P^-] = 0.15 \text{ M}$
Final concentrations	$[K^+] = 0.05 \text{ M} - x$	$[K^+] = 0.15 \text{ M} + x$
	$[Cl^-] = 0.05 \text{ M} - x$	$[Cl^-] = x$
		$[P^-] = 0.1 \text{ M}$

At equilibrium, the final concentration of KCl on each side of the membrane will be the same. This will allow us to solve for  $x$ .

$$(0.05 \text{ M} - x)^2 = (0.15 + x)x$$

$$0.0025 - 0.1x + \cancel{x^2} = 0.15x + \cancel{x^2}$$

$$0.0025 = 0.25x$$

$$x = 0.01$$

The final concentrations are thus,

	Left-hand Side	Right-hand Side
Final concentrations	$[K^+] = [Cl^-] = 0.05\text{ M} - 0.01\text{ M}$	$[K^+] = 0.15\text{ M} + 0.01\text{ M}$
	$[K^+] = [Cl^-] = 0.04\text{ M}$	$[K^+] = 0.16\text{ M}$
		$[Cl^-] = 0.01\text{ M}$

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# CHAPTER 8

## Electrochemical Cells

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LAIDLER . MEISER . SANCTUARY

# Physical Chemistry

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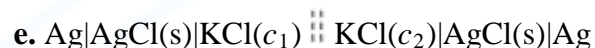
# Problems and Solutions

## Chapter 8

*\*problems with an asterisk are slightly more demanding*

## Electrode Reactions and Electrode Potentials

**8.1.** Write the electrode reactions, the overall reaction, and the expression for the emf for each of the following reversible cells.



[Solution](#)

**8.2.** At 25 °C and pH 7, a solution containing compound A and its reduced form  $\text{AH}_2$  has a standard electrode potential of  $-0.60 \text{ V}$ . A solution containing B and  $\text{BH}_2$  has a standard potential of  $-0.16 \text{ V}$ . If a cell were constructed with these systems as half-cells,

a. Would  $\text{AH}_2$  be oxidized by B or  $\text{BH}_2$  oxidized by A under standard conditions?

b. What would be the reversible emf of the cell?

c. What would be the effect of pH on the equilibrium ratio  $[\text{B}][\text{AH}_2]/[\text{A}][\text{BH}_2]$ ?

[Solution](#)

**8.3.** Calculate the standard electrode potential for the reaction  $\text{Cr}^{2+} + 2e^- \rightarrow \text{Cr}$  at 298 K. The necessary  $E^\circ$  values are



[Solution](#)

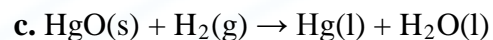
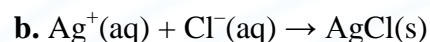
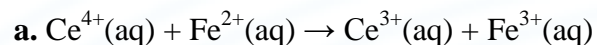
- 8.4. Write the individual electrode reactions and the overall cell reaction for the following cell:



where  $\text{F}^{2-}$  represents the fumarate ion and  $\text{S}^{2-}$  the succinate ion. Write the expression for the emf of the cell.

[Solution](#)

- 8.5. Design electrochemical cells in which each of the following reactions occurs:

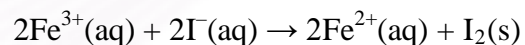


In each case, write the representation of the cell and the reactions at the two electrodes.

[Solution](#)

### Thermodynamics of Electrochemical Cells

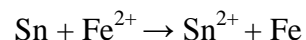
- 8.6. Calculate the equilibrium constant at 25 °C for the reaction



using the standard electrode potentials given in Table 8.1.

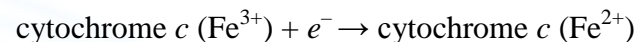
[Solution](#)

- 8.7. From data in Table 8.1, calculate the equilibrium constant at 25 °C for the reaction

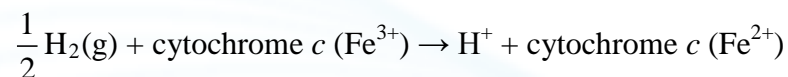


[Solution](#)

- 8.8.** The standard electrode potential at 25 °C for

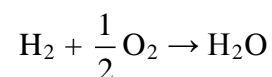


is 0.25 V. Calculate  $\Delta G^{\circ}$  for the process



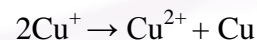
[Solution](#)

- 8.9.** Using the values given in Table 8.1, calculate the standard Gibbs energy change  $\Delta G^{\circ}$  for the reaction



[Solution](#)

- \*8.10.** From the data in Table 8.1, calculate the equilibrium constant at 25 °C for the reaction



What will be produced if  $\text{Cu}_2\text{O}$  is dissolved in dilute  $\text{H}_2\text{SO}_4$ ?

[Solution](#)

- 8.11.** For the reaction  $3\text{H}_2(\text{g}, 1 \text{ atm}) + \text{Sb}_2\text{O}_3(\text{s}, \text{cubic}) \rightarrow 2\text{Sb}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$ ,  $\Delta G^{\circ} = -83.7 \text{ kJ}$  [Roberts and Fenwick, *J. Amer. Chem. Soc.*, 50, 2146(1928)]. Calculate the potential developed by the cell



Which electrode will be positive?

[Solution](#)

**Nernst Equation and Nernst Potentials**

**8.12.** Calculate the emf for the following cell at 25 °C:

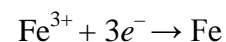


[Solution](#)

**8.13.** The pyruvate-lactate system has an  $E^{\circ'}$  value of  $-0.185 \text{ V}$  at 25 °C and pH 7.0. What will be the potential of this system if the oxidation has gone to 90% completion?

[Solution](#)

**8.14. a.** From the data in Table 8.1, calculate the standard electrode potential for the half-reaction



**b.** Calculate the emf at 25 °C of the cell



[Solution](#)

**8.15.** The cell  $\text{Pt}|\text{H}_2(1 \text{ bar}), \text{H}^+||\text{KCl}(\text{saturated})|\text{Hg}_2\text{Cl}_2|\text{Hg}$  was used to measure the pH of a solution of 0.010 *M* acetic acid in 0.0358 *M* sodium acetate. Calculate the cell potential expected at 25 °C [ $K_a = 1.81 \times 10^{-5}$  for acetic acid].

[Solution](#)

**8.16.** The voltage required to electrolyze certain solutions changes as the electrolysis proceeds because the concentrations in the solution are changing. In an experiment, 500 dm<sup>3</sup> of a 0.0500 *M* solution of copper (II) bromide was electrolyzed until 2.872 g Cu was deposited. Calculate the theoretical minimum voltage required to sustain the electrolysis reaction at the beginning and at the end of the experiment.

[Solution](#)

- 8.17.** Calculate the concentration of  $\text{I}_3^-$  in a standard solution of iodine in 0.5 *M* KI, making use of the following standard electrode potentials:



The molality of  $\text{I}^-$  in the standard solution can be assumed to be 0.5 *m*.

[Solution](#)

- 8.18.** Calculate the Nernst potential at 25 °C arising from the equilibrium established in Problem 7.41.

[Solution](#)

- 8.19.** It might seem plausible to separate lead and gold by making use of the great difference between their standard electrode potentials (Table 8.1). In order to test this idea, one might electrolyze a solution containing 0.0100 *M*  $\text{AuNO}_3$  and 0.0100 *M*  $\text{Pb}(\text{NO}_3)_2$  in a well-stirred tank using platinum electrodes at low current density. As the potential difference is slowly increased from zero, which metal will be deposited first? What will be the concentration of this metal ion in solution when the second metal begins to be deposited? Do you think this is an acceptable method of separating the two metals?

[Solution](#)

- 8.20.** Calculate the emf of the cell



[Solution](#)

- \*8.21.** Suppose that the cell in Problem 8.20 is set up but that the two solutions are separated by a membrane that is permeable to  $\text{H}^+$  ions but impermeable to  $\text{Cl}^-$  ions. What will be the emf of the cell at 25 °C?

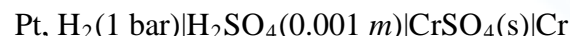
[Solution](#)

**\*8.22.** A typical biological cell has a volume of  $10^{-9} \text{ cm}^3$ , a surface area of  $10^{-6} \text{ cm}^2$ , and a membrane thickness of  $10^{-6} \text{ cm}$ ; the dielectric constant of the membrane may be taken as 3. Suppose that the concentration of  $\text{K}^+$  ions inside the cell is  $0.155 \text{ M}$  and that the Nernst potential across the cell wall is  $0.085 \text{ V}$ .

- Calculate the net charge on either side of the wall, and
- Calculate the fraction of the  $\text{K}^+$  ions in the cell that are required to produce this charge.

[Solution](#)

**\*8.23.** Calculate the emf at  $25^\circ \text{C}$  of the cell



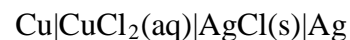
given the following standard electrode potential:



- First make the calculation neglecting activity coefficient corrections.
- Then make the calculation using activity coefficients estimated on the basis of the Debye-Hückel limiting law.

[Solution](#)

**\*8.24.** Write the individual electrode reactions and the overall reaction for



If the emf of the cell is  $0.191 \text{ V}$  when the concentration of  $\text{CuCl}_2$  is  $1.0 \times 10^{-4} \text{ M}$  and is  $-0.074 \text{ V}$  when the concentration is  $0.20 \text{ M}$ , make an estimate of the mean activity coefficient in the latter solution.

[Solution](#)

**\*8.25. a.** Write both electrode reactions and the overall reaction for the cell



**b.** Calculate  $E$  and  $E^\circ$  for this cell at 25 °C from the following information:



The solubility product for  $\text{TiCl}$  is  $1.6 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}$  at 25 °C.

[Solution](#)

**8.26.** Problem 7.44 involved calculating the concentrations on each side of a membrane after a Donnan equilibrium had become established. Which side of the membrane is positively charged? Calculate the Nernst potential across the membrane if the temperature is 37 °C.

[Solution](#)

**8.27.** The oxidation of lactate to pyruvate by the oxidized form of cytochrome  $c$ —represented as cytochrome  $c$  ( $\text{Fe}^{3+}$ )—is an important biological reaction. The following are the relevant  $E^\circ$  values, relating to pH 7 and 25 °C:

	$E^\circ/\text{V}$
pyruvate $^-$ + 2H $^+$ + 2e $^-$ → lactate $^-$	−0.185
cytochrome $c$ ( $\text{Fe}^{3+}$ ) + e $^-$ → cytochrome $c$ ( $\text{Fe}^{2+}$ )	0.254

Calculate the equilibrium ratio

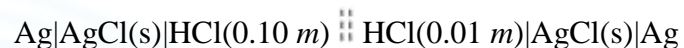
$$\frac{[\text{cytochrome } c (\text{Fe}^{2+})]^2 [\text{pyruvate}^-]}{[\text{cytochrome } c (\text{Fe}^{3+})]^2 [\text{lactate}^-]}$$

at pH 7 and 25 °C. Also calculate the ratio at pH 6.

[Solution](#)



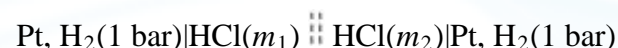
**8.28.** Suppose that the cell



is set up and that the membrane separating the two solutions is permeable only to  $\text{H}^+$  ions. What is the emf of the cell at  $25\text{ }^\circ\text{C}$ ?

[Solution](#)

**8.29. a.** Consider the cell

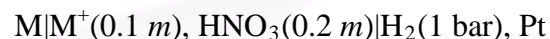


in which the solutions are separated by a partition that is permeable to both  $\text{H}^+$  and  $\text{Cl}^-$ . The ratio of the speeds with which these ions pass through the membrane is the ratio of their transport numbers  $t_+$  and  $t_-$ . Derive an expression for the emf of this cell.

**b.** If when  $m_1 = 0.01\text{ }m$  and  $m_2 = 0.01\text{ }m$  the emf is  $0.0190\text{ V}$ , what are the transport numbers of the  $\text{H}^+$  and  $\text{Cl}^-$  ions?

[Solution](#)

**8.30.** The metal M forms a soluble nitrate and a very slightly soluble chloride. The cell



has a measured  $E = -0.40\text{ V}$  at  $298.15\text{ K}$ . When sufficient solid KCl is added to make the solution of the cell  $0.20\text{ }m$  in  $\text{K}^+$ , the emf changes to  $-0.15\text{ V}$  at  $298.15\text{ K}$  as MCl precipitates. Calculate the  $K_{\text{sp}}$  of MCl, taking all activity coefficients to be unity.

[Solution](#)

- 8.31.** The substance nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) plays an important role in biological systems; under the action of certain enzymes it can react with a reducing agent and release a proton to the solution to form its reduced form NADH. With pyruvate the reduced form NADH undergoes the reaction



The appropriate  $E^\circ'$  values, relating to 25 °C and pH 7, are



Use these values to calculate  $\Delta G^\circ'$  for the reaction, and also the equilibrium ratio

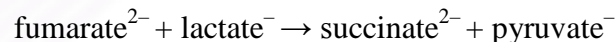
$$\frac{[\text{lactate}^-][\text{NAD}^+]}{[\text{pyruvate}^-][\text{NADH}]}$$

(a) at pH 7, and (b) at pH 8.

[Solution](#)

### Temperature Dependence of Cell emfs

- 8.32.** a. Calculate the standard emf  $E^\circ$  for the reaction



on the basis of the following information:

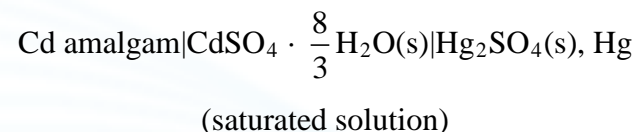


The  $E^\circ'$  values relate to pH 7. The temperature coefficient  $\partial E/\partial T$  for this cell is  $2.18 \times 10^{-5} \text{ V K}^{-1}$ .

- b. Calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 25 °C.

[Solution](#)

**8.33.** The Weston standard cell (see Figure 8.2b) is

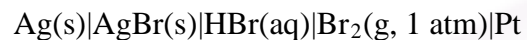


**a.** Write the cell reaction.

**b.** At 25 °C, the emf is 1.018 32 V and  $\partial E^\circ / \partial T = -5.00 \times 10^{-5} \text{ V K}^{-1}$ . Calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ .

[Solution](#)

**8.34.** Salstrom and Hildebrand [*J. Amer. Chem. Soc.*, 52, 4650(1930)] reported the following data for the cell



$t/^\circ\text{C}$	442.3	456.0	490.9	521.4	538.3	556.2
$E/\text{V}$	0.8031	0.7989	0.7887	0.7803	0.7751	0.7702

Find the temperature coefficient for this cell assuming a linear dependence of the cell potential with temperature. What is the entropy change for the cell reaction?

[Solution](#)

**8.35.** The reaction taking place in the cell  $\text{Mg(s)} | \text{Mg}^{2+}(\text{aq}), \text{Cl}^-(\text{aq}) | \text{Cl}_2(\text{g}, 1 \text{ atm}) | \text{Pt}$  is found to have an entropy change of  $-337.3 \text{ J K}^{-1} \text{ mol}^{-1}$  under standard conditions. What is the temperature coefficient for the cell?

[Solution](#)

**\*8.36. a.** Estimate the Gibbs energy of formation of the fumarate ion, using data in Problem 8.32 and the following values.

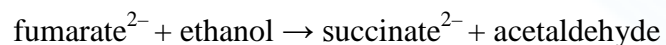
$$\Delta_f G^\circ (\text{succinate, aq}) = -690.44 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ (\text{acetaldehyde, aq}) = 139.08 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ (\text{ethanol, aq}) = -181.75 \text{ kJ mol}^{-1}$$

$$\text{acetaldehyde} + 2\text{H}^+ + 2e^- \rightarrow \text{ethanol} \quad E^\circ = -0.197 \text{ V}$$

**b.** If the  $\partial E^\circ / \partial T$  value for the process



is  $1.45 \times 10^{-4} \text{ V K}^{-1}$ , estimate the enthalpy of formation of the fumarate ion from the following values.

$$\Delta_f H^\circ (\text{succinate, aq}) = -908.68 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{acetaldehyde, aq}) = -210.66 \text{ kJ mol}^{-1}$$

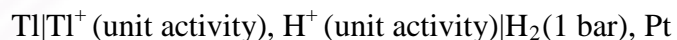
$$\Delta_f H^\circ (\text{ethanol, aq}) = -287.02 \text{ kJ mol}^{-1}$$

[Solution](#)

**\*8.37. a.** Calculate the emf at 298.15 K for the cell



**b.** Calculate  $\Delta H$  for the cell reaction in the following cell.



For the half-cell

$$\text{Tl}^+ + e^- \rightarrow \text{Tl} \quad E^\circ = 0.34 \text{ V}$$

$$\partial E / \partial T = -0.003 \text{ V/K and}$$

$$K_{\text{sp}}(\text{TlBr}) = 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$$

[Solution](#)

## Applications of emf Measurements

**8.38.** Calculate the solubility product and the solubility of AgBr at 25 °C on the basis of the following standard electrode potentials:

[Solution](#)

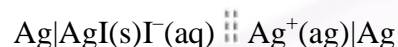
**8.39.** The emf of a cell



was found to be 0.517 V at 25 °C. Calculate the pH of the HCl solution.

[Solution](#)

**8.40.** The emf of the cell



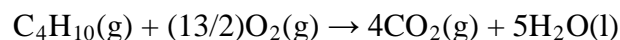
is –0.9509 V at 25 °C. Calculate the solubility and the solubility product of AgI at that temperature.

[Solution](#)

**8.41.** An electrochemical cell  $\text{M(s)}|\text{MCl(aq, 1.0 } m)|\text{AgCl(s)}|\text{Ag(s)}$ , where MCl is the chloride salt of the metal electrode M, yields a cell potential of 0.2053 V at 25 °C. What is the mean activity coefficient  $\gamma_{\pm}$  of the electrolyte MCl?  $E^\circ$  for the  $\text{M(s)}|\text{M}^+$  electrode is 0.0254 V.

[Solution](#)

**8.42.** The following thermodynamic data apply to the complete oxidation of butane at 25 °C.



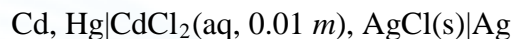
$$\Delta H^\circ = -2877 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -432.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

Suppose that a completely efficient fuel cell could be set up utilizing this reaction. Calculate (a) the maximum electrical work and (b) the maximum total work that could be obtained at 25 °C.

[Solution](#)

**\*8.43.** At 298 K the emf of the cell

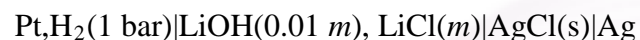


is 0.7585 V. The standard emf of the cell is 0.5732 V.

- Calculate the mean activity coefficient for the  $\text{Cd}^{2+}$  and  $\text{Cl}^-$  ions.
- Compare the value with that estimated from the Debye-Hückel limiting law, and comment on any difference.

[Solution](#)

**\*8.44.** The following emf values were obtained by H. S. Harned and Copson [*J. Amer. Chem. Soc.*, 55, 2206(1933)] at 25 °C for the cell



at various molalities  $m$  of LiCl:

$m/\text{mol kg}^{-1}$	0.01	0.02	0.05	0.10	0.20
$E/\text{V}$	1.0498	1.0318	1.0076	1.9888	0.9696

Obtain from these data the ionic product of water.

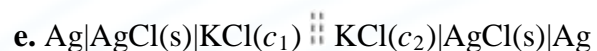
[Solution](#)

### Essay Questions

- Explain how emf measurements can be used to obtain  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for a reaction.
- Suggest an additional example, giving details, for each of the electrochemical cells listed in Figure 8.8.

**Solutions**

**8.1.** Write the electrode reactions, the overall reaction, and the expression for the emf for each of the following reversible cells.

**Solution:**

Given: see above

Required: electrode reactions, the overall reaction, and the expression for the emf

We calculate the emf, or electromotive force, from Eq. 8.13

$$E = E^\circ - \frac{RT}{zF} \ln \left( \frac{\cdots [Y]^y [Z]^z}{[A]^a [B]^b \cdots} \right)^u \text{ where } z \text{ is the number of electrons.}$$

Electrode reactions	Overall reaction	EMF
$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$ $\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{H}^+ + 2\text{Cl}^-$ $z = 2$	$E = E^\circ - \frac{RT}{2F} \ln \left( [\text{H}^+]^2 [\text{Cl}^-]^2 \right)^u$
$2\text{Hg}(l) + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2e^-$ $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	$2\text{Hg}(l) + 2\text{Cl}^- + 2\text{H}^+ \rightarrow \text{Hg}_2\text{Cl}_2 + \text{H}_2$ $z = 2$	$E = E^\circ - \frac{RT}{2F} \ln \left( \frac{1}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right)^u$ $E = E^\circ + \frac{RT}{2F} \ln \left( [\text{H}^+]^2 [\text{Cl}^-]^2 \right)^u$

$\text{Ag(s)} + \text{Cl}^- \rightarrow \text{AgCl(s)} + e^-$ $\text{Hg}_2\text{Cl}_2(\text{s}) + 2e^- \rightarrow 2\text{Hg(s)} + 2\text{Cl}^-$	$2\text{Ag(s)} + \text{Hg}_2\text{Cl}_2(\text{s}) \rightarrow 2\text{AgCl(s)} + 2\text{Hg(s)}$ $z = 2$	No concentration dependence, therefore $E = E^\circ$
$\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H}^+ + e^-$ $\text{AuI(s)} + e^- \rightarrow \text{Au(s)} + \text{I}^-$	$\text{AuI(s)} + \frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{Au(s)} + \text{H}^+ + \text{I}^-$ $z = 1$	$E = E^\circ - \frac{RT}{F} \ln \left( [\text{H}^+][\text{I}^-] \right)^u$
$\text{Ag(s)} + \text{Cl}^-(c_1) \rightarrow \text{AgCl(s)} + e^-$ $\text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^-(c_2)$	$\text{Cl}^-(c_1) \rightarrow \text{Cl}^-(c_2)$ $z = 1$	$E = E^\circ - \frac{RT}{F} \ln \left( \frac{c_1}{c_2} \right)^u$

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**8.2.** At 25 °C and pH 7, a solution containing compound A and its reduced form  $\text{AH}_2$  has a standard electrode potential of  $-0.60 \text{ V}$ . A solution containing B and  $\text{BH}_2$  has a standard potential of  $-0.16 \text{ V}$ . If a cell were constructed with these systems as half-cells,

- Would  $\text{AH}_2$  be oxidized by B or  $\text{BH}_2$  oxidized by A under standard conditions?
- What would be the reversible emf of the cell?
- What would be the effect of pH on the equilibrium ratio  $[\text{B}][\text{AH}_2]/[\text{A}][\text{BH}_2]$ ?

**Solution:**

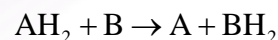
Given:  $T = 25 \text{ }^\circ\text{C}$ ,  $\text{pH} = 7$ ,  $E^\circ_{\text{A}} = -0.60 \text{ V}$ ,  $E^\circ_{\text{B}} = -0.16 \text{ V}$

Required: see above

- a. The reduction potential for each half reaction is:



We reverse the first reaction since we require a positive potential for the overall reaction to be spontaneous in the forward direction. Therefore  $\text{AH}_2$  is oxidized.



- b. The reversible emf would be

$$E = E^\circ_{\text{B}} - E^\circ_{\text{A}}$$

$$E = -0.16 \text{ V} - (-0.60 \text{ V})$$

$$\boxed{E = 0.44 \text{ V}}$$

- c. The equilibrium ratio is given by  $K = \frac{[\text{B}][\text{AH}_2]}{[\text{A}][\text{BH}_2]}$ . There is no dependence of  $[\text{H}_3\text{O}^+]$  in the equilibrium expression, and the hydrogen-containing entities cancel in the numerator and denominator. As a result, there is no effect of pH on the equilibrium ratio.

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**8.3.** Calculate the standard electrode potential for the reaction  $\text{Cr}^{2+} + 2e^- \rightarrow \text{Cr}$  at 298 K. The necessary  $E^\circ$  values are



**Solution:**

Given: see above

Required:  $E^\circ$  for  $\text{Cr}^{2+}$

To solve this problem, we follow Example 8.3.

We first calculate the  $\Delta G^\circ$  values for these two reactions using Eq. 8.2

$$\Delta G^\circ = -zFE^\circ$$

$$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr} \quad \Delta G_1^\circ = -3 \times 96\,485 \text{ J mol}^{-1} \times (-0.74 \text{ V}) = 2.22 \text{ V} \times 96\,485 \text{ J mol}^{-1} \quad (1)$$

$$\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+} \quad \Delta G_2^\circ = -1 \times 96\,485 \text{ J mol}^{-1} \times (-0.41 \text{ V}) = 0.41 \text{ V} \times 96\,485 \text{ J mol}^{-1} \quad (2) \text{ The reaction } \text{Cr}^{2+} + 2e^- \rightarrow \text{Cr} \text{ is obtained}$$

by subtracting reaction (2) from reaction (1), and the  $\Delta G^\circ$  for this reaction is obtained from by subtracting  $\Delta G_2^\circ$  from  $\Delta G_1^\circ$ .

$$\Delta G^\circ = \Delta G_1^\circ - \Delta G_2^\circ$$

$$\Delta G^\circ = 2.22 \text{ V} \times 96\,485 \text{ J mol}^{-1} - 0.41 \text{ V} \times 96\,485 \text{ J mol}^{-1}$$

$$\Delta G^\circ = 1.81 \text{ V} \times 96\,485 \text{ J mol}^{-1}$$

$$\Delta G^\circ = 1.81 \text{ V} \times F$$

We solve for  $E^\circ$  by rearranging Eq. 8.2 and setting  $z = 2$ .

$$E^\circ = \frac{\Delta G^\circ}{-zF}$$

$$E^\circ = \frac{1.81 \text{ V} \cancel{F}}{-2 \cancel{F}}$$

$$E^\circ = -0.905 \text{ V}$$

$$\boxed{E^\circ = -0.91 \text{ V}}$$

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**8.4.** Write the individual electrode reactions and the overall cell reaction for the following cell:

$\text{Pt, H}_2 | \text{H}^+(1\text{ m}) || \text{F}^{2-}, \text{S}^{2-}, \text{H}^+(\text{aq}) | \text{Pt}$

where  $\text{F}^{2-}$  represents the fumarate ion and  $\text{S}^{2-}$  the succinate ion. Write the expression for the emf of the cell.

**Solution:**

Given: see above

Required:  $E$

We first write down the half reactions that are occurring in this cell.

LHS electrode  $\text{H}_2 \rightarrow 2\text{H}^+(1\text{ m}) + 2e^-$

RHS electrode  $2e^- + 2\text{H}^+(\text{aq}) + \text{F}^{2-} \rightarrow \text{S}^{2-}$

The overall reaction is,

$2\text{H}^+(\text{aq}) + \text{F}^{2-} + \text{H}_2 \rightarrow 2\text{H}^+(1\text{ m}) + \text{S}^{2-}$

The expression for the emf of the cell is determined from Eq. 8.13,

$$E = E^\circ - \frac{RT}{zF} \ln \left( \frac{\cdots [\text{Y}]^y [\text{Z}]^z}{[\text{A}]^a [\text{B}]^b \cdots} \right)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln \left( \frac{[\text{S}^{2-}][\text{H}^+]^2}{[\text{F}^{2-}][\text{H}_{\text{aq}}^+]^2} \right)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln \left( \frac{[\text{S}^{2-}](1\text{ m})^2}{[\text{F}^{2-}][\text{C}]^2} \right)$$

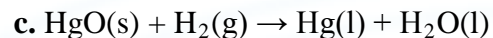
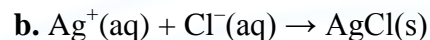
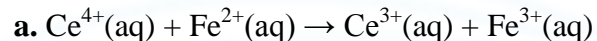
Where  $[\text{H}^+]=\text{C}$  is the concentration of  $[\text{H}^+]$  on the LHS.

We drop the superscript  $u$  since we have numerical values for the concentration.

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**8.5.** Design electrochemical cells in which each of the following reactions occurs:



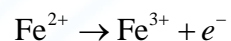
In each case, write the representation of the cell and the reactions at the two electrodes.

**Solution:**

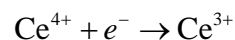
Given: see above

Required: design the electrochemical cells

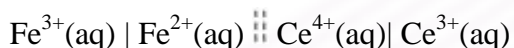
- a. In writing the representation of the cell, the oxidation reaction always occurs at the anode, which is placed at the left-hand position of the cell. In this case,  $\text{Fe}^{2+}$  is losing electrons, and therefore the oxidation process is:



The cathode reaction is written on the right-hand side of the cell and is:



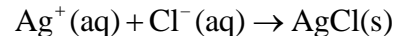
This is where reduction occurs. The overall reaction is the sum of these two reactions. The cell representation is:



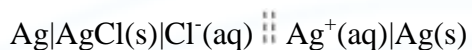
- b. Upon examining the standard reduction potentials in Table 8.1, we see that the following half reactions can be combined to give the cited reaction.



Reversal of equation (2), and then addition to equation (1) gives the overall desired equation:



Equation (1) is the reduction reaction and is placed on the right-hand side of the cell. The anode reaction is placed on the left-hand side of the cell representation.



The voltage of this cell is the right-hand reduction potential minus the left-hand reduction potential.

$$E^\circ = E_1^\circ - E_2^\circ$$

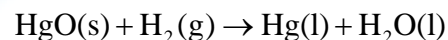
$$E^\circ = 0.7996 \text{ V} - 0.22233 \text{ V}$$

$$E^\circ = 0.57727 \text{ V}$$

c. HgO undergoes reduction to Hg and is the cathode. H<sub>2</sub> is oxidized and is the anode. The electrode potentials are obtained from Table 8.1 and the SRP Table.



Reversing the sense of equation (3) and adding to (4) gives,



The cell is represented by



The cell potential is

$$E^\circ = E_4^\circ - E_3^\circ$$

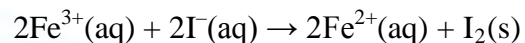
$$E^\circ = 0.0977 \text{ V} - (-0.8277 \text{ V})$$

$$E^\circ = 0.9254 \text{ V}$$

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**8.6.** Calculate the equilibrium constant at 25 °C for the reaction



using the standard electrode potentials given in Table 8.1.

**Solution:**

Given: Table 8.1

Required:  $K$

We can calculate the equilibrium constant from Eq. 8.7

$$E^{\circ} / \text{V} = \frac{0.0257}{z} \ln K^{\circ}$$

$$K^{\circ} = \exp\left(\frac{z(E^{\circ} / \text{V})}{0.0257}\right)$$

The half cell reactions are



And the overall emf is

$$E^{\circ} = 0.771 \text{ V} - 0.5355 \text{ V}$$

$$E^{\circ} = 0.2355 \text{ V}$$

We solve for  $K$  with  $z = 2$ ,

$$K^{\circ} = \exp\left(\frac{2(0.2355)}{0.0257}\right)$$

$$K^{\circ} = \exp(18.32684825)$$

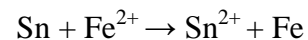
$$K^{\circ} = 91\,043\,525.2$$

$$\boxed{K^{\circ} = 9.10 \times 10^7}$$

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**8.7.** From data in Table 8.1, calculate the equilibrium constant at 25 °C for the reaction



**Solution:**

Given: Table 8.1

Required:  $K$

We follow the same procedure as we did in problem 8.6 to solve for the equilibrium constant.

The half cell reactions are



The overall emf is

$$E^{\circ} = -0.447 \text{ V} - (-0.1375 \text{ V})$$

$$E^{\circ} = -0.3095 \text{ V}$$

Solving for  $K$  with  $z = 2$  gives,

$$K^{\circ} = \exp\left(\frac{2(-0.3095)}{0.0257}\right)$$

$$K^{\circ} = \exp(-24.08560311)$$

$$K^{\circ} = 3.46\,541\,679 \times 10^{-11}$$

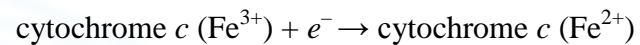
$$\boxed{K^{\circ} = 3.47 \times 10^{-11}}$$

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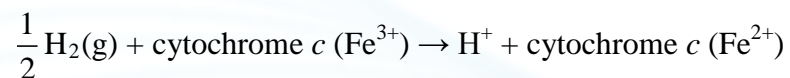
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**8.8.** The standard electrode potential at 25 °C for



is 0.25 V. Calculate  $\Delta G^{\circ}$  for the process



**Solution:**

Given:  $E^{\circ} = 0.25 \text{ V}$

Required:  $\Delta G^{\circ}$

We calculate  $\Delta G^{\circ}$  for this reaction using Eq. 8.2,

$$\Delta G^{\circ} = -zFE^{\circ}, \text{ where } z = 1$$

$$\Delta G^{\circ} = -1 \times 96\,485 \text{ mol}^{-1} \times 0.25 \text{ J}$$

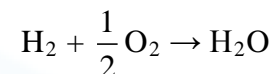
$$\Delta G^{\circ} = -24\,121.25 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^{\circ} = -24 \text{ kJ mol}^{-1}}$$

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**8.9.** Using the values given in Table 8.1, calculate the standard Gibbs energy change  $\Delta G^\circ$  for the reaction



**Solution:**

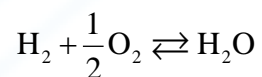
Given: Table 8.1

Required:  $\Delta G^\circ$

From Table 8.1, we write the following half reactions:



Subtracting (2) from  $\frac{1}{2}$  of (1) gives the desired equation,



The overall emf is

$$E^\circ = 1.229 \text{ V} - 0$$

$$E^\circ = 1.229 \text{ V}$$

We calculate  $\Delta G^\circ$  for this reaction using Eq. 8.2,

$$\Delta G^\circ = -zFE, \text{ where } z=2$$

$$\Delta G^\circ = -2 \times 96\,485 \text{ mol}^{-1} \times 1.229 \text{ J}$$

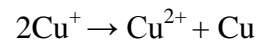
$$\Delta G^\circ = -237\,160.13 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^\circ = -237.2 \text{ kJ mol}^{-1}}$$

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**\*8.10.** From the data in Table 8.1, calculate the equilibrium constant at 25 °C for the reaction



What will be produced if  $\text{Cu}_2\text{O}$  is dissolved in dilute  $\text{H}_2\text{SO}_4$ ?

**Solution:**

Given: Table 8.1

Required:  $K$

We follow the same procedure as we did in problem 8.6 to solve for the equilibrium constant.

From Table 8.1, we write the following half reactions:



To get the desired overall reaction, we subtract  $2 \times (2)$  from (1):



$$E^\circ = E_1^\circ - E_2^\circ$$

$$E^\circ = 0.3419 \text{ V} - 0.153 \text{ V}$$

$$E^\circ = 0.1889 \text{ V}$$

We solve for  $K$  from Eq. 8.7, with  $z = 2$ ,

$$K^\circ = \exp\left(\frac{2(0.1889)}{0.0257}\right)$$

$$K^\circ = 2\,422\,690.131$$

$$\boxed{K^\circ = 2.42 \times 10^6}$$

If  $\text{Cu}_2\text{O}$  is dissolved in dilute  $\text{H}_2\text{SO}_4$ , then half will form  $\text{Cu}^{2+}$  and half will form  $\text{Cu}$ .

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**8.11.** For the reaction  $3\text{H}_2(\text{g}, 1 \text{ atm}) + \text{Sb}_2\text{O}_3(\text{s, cubic}) \rightarrow 2\text{Sb}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$ ,  $\Delta G^\circ = -83.7 \text{ kJ}$  [Roberts and Fenwick, *J. Amer. Chem. Soc.*, 50, 2146(1928)]. Calculate the potential developed by the cell



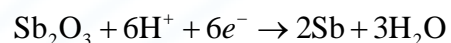
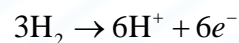
Which electrode will be positive?

**Solution:**

Given: reaction above,  $\Delta G^\circ = -83.7 \text{ kJ}$

Required:  $E^\circ$ , positive electrode

Note that the  $\Delta G^\circ$  given is for the reaction of 3 moles of  $\text{H}_2$  to form 2 moles of Sb. The half cell reactions may be written as,



We can solve for  $E^\circ$  using Eq. 8.2,

$$\Delta G^\circ = -zFE$$

$$\Delta E^\circ = \frac{\Delta G^\circ}{-zF}$$

$$\Delta E^\circ = \frac{-83.7 \times 10^3 \text{ J}}{-6 \times 96485}$$

$$\Delta E^\circ = 0.1445820594 \text{ V}$$

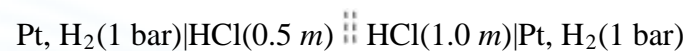
$$\boxed{\Delta E^\circ = 0.145 \text{ V}}$$

For this reaction to be spontaneous, the electron flow is from the hydrogen electrode (oxidation) to the antimony electrode (reduction).

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**8.12.** Calculate the emf for the following cell at 25 °C:



**Solution:**

Given:  $T = 25 \text{ }^\circ\text{C}$ , cell above

Required:  $E$

We calculate the emf for the cell from Eq. 8.27 where  $z = 1$ ,

$$E = \frac{RT}{F} \ln \frac{m_2}{m_1}$$

$$E = 0.0257 \ln \frac{1.0 \text{ m}}{0.5 \text{ m}}$$

$$E = 0.0178138825 \text{ V}$$

$$\boxed{E = 0.018 \text{ V}}$$

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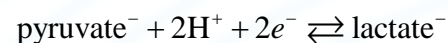
**8.13.** The pyruvate-lactate system has an  $E^{\circ'}$  value of  $-0.185$  V at  $25$  °C and pH 7.0. What will be the potential of this system if the oxidation has gone to 90% completion?

**Solution:**

Given:  $E^{\circ'} = -0.185$  V, pH = 7.0, 90% completion

Required:  $E$

The process is,



And, the Nernst equation, given by Eq. 8.13

$$E = E^{\circ} - \frac{RT}{zF} n \left( \frac{...[\text{Y}]^y [\text{Z}]^z}{[\text{A}]^a [\text{B}]^b ...} \right)^u$$

For this process, this becomes

$$E = E^{\circ} - \frac{RT}{2F} \ln \left( \frac{[\text{lactate}^-]}{[\text{pyruvate}^-]} \right)$$

Solving for  $E$  we get,

$$E = -0.185 \text{ V} - \frac{0.0257}{2} \ln \left( \frac{10}{90} \right)$$

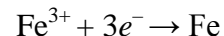
$$E = -0.156 \text{ 765 664 2 V}$$

$$\boxed{E = -0.157 \text{ V}}$$

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**8.14. a.** From the data in Table 8.1, calculate the standard electrode potential for the half-reaction



**b.** Calculate the emf at 25 °C of the cell



**Solution:**

Given: Table 8.1

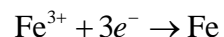
Required: see above

a. To calculate the standard potential we follow example 8.3.  
We first calculate the  $\Delta G^{\circ}$  values for these two reactions using Eq. 8.2

$$\Delta G^{\circ} = -zFE$$

$$\text{Fe}^{3+} + e^{-} \rightarrow \text{Fe}^{2+} \quad \Delta G_1^{\circ} = -1 \times 96\,485\text{ J mol}^{-1} \times (0.771\text{ V}) = -0.771\text{ V} \times 96\,485\text{ J mol}^{-1} \quad (1)$$

$$\text{Fe}^{2+} + 2e^{-} \rightarrow \text{Fe} \quad \Delta G_2^{\circ} = -2 \times 96\,485\text{ J mol}^{-1} \times (-0.447\text{ V}) = 0.894\text{ V} \times 96\,485\text{ J mol}^{-1} \quad (2)$$



The half-reaction given above is the sum of (1) and (2). The  $\Delta G^{\circ}$  value for the given reaction is

$$\Delta G^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

$$\Delta G^{\circ} = -0.771\text{ V} \times 96\,485\text{ J mol}^{-1} + 0.894\text{ V} \times 96\,485\text{ J mol}^{-1}$$

$$\Delta G^{\circ} = 0.123\text{ V} \times 96\,485\text{ J mol}^{-1}$$

$$\Delta G^{\circ} = 0.123\text{ V} \times F$$

We solve for  $E^{\circ}$  by rearranging Eq. 8.2 and setting  $z = 3$ .

$$E^{\circ} = \frac{\Delta G^{\circ}}{-zF}$$

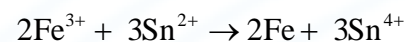
$$E^{\circ} = \frac{0.123 \text{ V}}{-3}$$

$$E^{\circ} = -0.041 \text{ V}$$

b. The half cell reactions are:



The overall reaction is obtained from the sum of  $2 \times (3)$  and  $3 \times (4)$



The electrical potential would be,

$$E^{\circ} = E_3^{\circ} + E_4^{\circ}$$

$$E^{\circ} = -0.041 \text{ V} - 0.151 \text{ V}$$

$$E^{\circ} = -0.192 \text{ V}$$

From the Nernst equation, Eq. 8.13 we can calculate the emf using  $z = 6$ .

$$E = E^{\circ} - \frac{RT}{zF} \ln \left( \frac{[\dots][Y]^y[Z]^z}{[A]^a[B]^b \dots} \right)^u$$

$$E = -0.192 - \frac{0.0257}{6} \ln \left( \frac{(0.01)^3}{(0.1)^3 (0.5)^2} \right)$$

$$E = -0.168 \text{ 349 742 4 V}$$

$$\boxed{E = -0.17 \text{ V}}$$

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**8.15.** The cell  $\text{Pt}|\text{H}_2(1 \text{ bar}), \text{H}^+ || \text{KCl}(\text{saturated})|\text{Hg}_2\text{Cl}_2|\text{Hg}$  was used to measure the pH of a solution of  $0.010 \text{ M}$  acetic acid in  $0.0358 \text{ M}$  sodium acetate. Calculate the cell potential expected at  $25^\circ\text{C}$  [ $K_a = 1.81 \times 10^{-5}$  for acetic acid].

**Solution:**

Given:  $c_{\text{acetic acid}} = 0.010 \text{ M}$ ,  $c_{\text{sodium acetate}} = 0.0358 \text{ M}$ ,  $T = 25^\circ\text{C}$ ,  $K_a = 1.81 \times 10^{-5}$

Required:  $E$

The equilibrium constant,  $K_a$  is given by,

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Rearranging for  $[\text{H}^+]$ , we obtain

$$[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] = \frac{(1.81 \times 10^{-5})(0.010 \text{ M})}{(0.0358 \text{ M})}$$

$$[\text{H}^+] = 5.055865922 \times 10^{-6}$$

From Table 8.1, the cell reactions are:



However, since the cathode reaction (the reduction reaction), is contained in the standard calomel ( $\text{Hg}_2\text{Cl}_{2(\text{s})}$ ) electrode, it is separated from the oxidation of  $\text{H}_2$ , and its concentrations are constant throughout the measurement. This is a pH meter, so the only concentration that is relevant is  $[\text{H}^+]$ .

$$E = E^\circ - \frac{RT}{2F} \ln [\text{H}^+]^2$$

$$E^\circ = 0 + 0.2412 \text{ V}$$

$$E = 0.2412 \text{ V} - \frac{0.0257}{2} \ln (5.055\,865\,922 \times 10^{-6})^2$$

$$E = 0.554\,610\,508\,5 \text{ V}$$

$$\boxed{E = 0.55 \text{ V}}$$

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**8.16.** The voltage required to electrolyze certain solutions changes as the electrolysis proceeds because the concentrations in the solution are changing. In an experiment, 500 dm<sup>3</sup> of a 0.0500 M solution of copper (II) bromide was electrolyzed until 2.872 g Cu was deposited. Calculate the theoretical minimum voltage required to sustain the electrolysis reaction at the beginning and at the end of the experiment.

**Solution:**

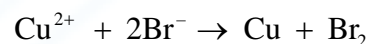
Given:  $V = 500 \text{ dm}^3$ ,  $[\text{Cu}^{2+}] = 0.0500 \text{ M}$ ,  $[\text{Br}^-] = 0.100 \text{ M}$ ,  $m_{\text{Cu}} = 2.872 \text{ g}$

Required:  $E_i$ ,  $E_f$

The reactions taking place during the electrolysis are:



The overall reaction is:



The electrical potential would be the sum of the two potentials,

$$E^\circ = 0.34190 \text{ V} - 1.08730 \text{ V}$$

$$E^\circ = -0.74540 \text{ V}$$

If the *reverse* reaction were taking place in a galvanic cell, the initial cell voltage would be:

$$E = E^\circ - \frac{RT}{2F} \ln [\text{Cu}^{2+}] [\text{Br}^-]^2$$

$$E^\circ = 0.74540 \text{ V}$$

$$E_i = 0.74540 \text{ V} - \frac{0.0257}{2} \ln (0.0500)(0.100)^2$$

$$E_i = 0.8430715966 \text{ V}$$

$$\boxed{E_i = 0.84307 \text{ V}}$$

Therefore a minimum voltage of 0.84 307 V would have to be applied at the beginning in order for the electrolysis reaction to occur.

At the end of the electrolysis, the concentrations are:

$$[\text{Cu}^{2+}] = 0.0500 \text{ M} - \left( \frac{m_{\text{Cu}}}{M_{\text{Cu}}} \times \frac{1}{V} \right)$$

$$[\text{Cu}^{2+}] = 0.0500 \text{ M} - \frac{2.872 \text{ g}}{(63.456 \text{ g mol}^{-1})(500 \text{ dm}^3)}$$

$$[\text{Cu}^{2+}] = 0.0500 \text{ M} - 9.051\,941\,503 \times 10^{-5} \text{ M}$$

$$[\text{Cu}^{2+}] = 0.049\,909\,480\,6 \text{ M}$$

$$[\text{Br}^-] = 0.100 \text{ M} - 2 \times 9.051\,941\,503 \times 10^{-5} \text{ M}$$

$$[\text{Br}^-] = 0.099\,818\,961\,2 \text{ M}$$

Therefore the final voltage required would be

$$E_f = 0.74540 \text{ V} - \frac{0.0257}{2} \ln(0.0\,499\,094\,806 \text{ M})(0.0\,998\,189\,612)^2$$

$$E_f = 0.8\,431\,414\,503 \text{ V}$$

$$\boxed{E_f = 0.84\,314 \text{ V}}$$

The  $E_i$  and  $E_f$  are close because a small amount of  $\text{Cu}^{2+}$  is plated out.

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**8.17.** Calculate the concentration of  $\text{I}_3^-$  in a standard solution of iodine in  $0.5\text{ M KI}$ , making use of the following standard electrode potentials:



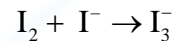
The molality of  $\text{I}^-$  in the standard solution can be assumed to be  $0.5\text{ m}$ .

**Solution:**

Given:  $c_{\text{KI}} = 0.5\text{ M}$

Required:  $c_{\text{I}_3^-}$

The overall reaction of interest is obtained by reversing the second equation and adding it to the first.



In this case,  $z = 2$ , and the standard electrode potential is

$$E^\circ = 0.5355\text{ V} - 0.5365\text{ V}$$

$$E^\circ = -0.0010\text{ V}$$

We can solve for the concentration of  $\text{I}_3^-$  using Eq. 8.7, where the equilibrium constant for this process is given by,

$$K_c = \frac{[\text{I}_3^-]}{[\text{I}^-]}$$

$$E^\circ / V = \frac{0.0257}{z} \ln K^\circ$$

$$K^\circ = \exp\left(\frac{z(E^\circ / V)}{0.0257}\right)$$

$$\frac{[\text{I}_3^-]}{[\text{I}^-]} = \exp\left(\frac{z(E^\circ / V)}{0.0257}\right)$$

$$c_{\text{I}_3^-} = c_{\text{I}^-} \exp\left(\frac{z(E^\circ / V)}{0.0257}\right)$$

$$c_{\text{I}_3^-} = (0.5 \text{ mol dm}^{-3}) \exp\left(\frac{2(-0.0010)}{0.0257}\right)$$

$$c_{\text{I}_3^-} = 0.4625649996 \text{ mol dm}^{-3}$$

$$\boxed{c_{\text{I}_3^-} = 0.4626 \text{ mol dm}^{-3}}$$

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**8.18.** Calculate the Nernst potential at 25 °C arising from the equilibrium established in Problem 7.41.

**Solution:**

Given: Problem 7.41,  $T = 25\text{ °C}$

Required:  $\Delta\Phi$  ( $\Delta\Phi = \Delta E^\circ$  for concentration cells)

The Nernst potential is given by Eq. 8.19 as,

$$\Delta\Phi = \frac{RT}{zF} \ln \frac{c_1}{c_2}$$

From problem 7.41, we have the equilibrium concentrations of sodium and chloride as,

Palmitate side	Other side
$[\text{Na}^+] = 0.18\text{ M}$	$[\text{Na}^+] = 0.12\text{ M}$
$[\text{Cl}^-] = 0.08\text{ M}$	$[\text{Cl}^-] = 0.12\text{ M}$

To calculate the Nernst potential, we only consider the  $\text{Na}^+$  equilibrium, therefore,

$$\Delta\Phi = 0.0257 \ln \frac{0.18\text{ M}}{0.12\text{ M}}$$

$$\Delta\Phi = 0.010\,420\,453\,3\text{ V}$$

$$\boxed{\Delta\Phi = 10\text{ mV}}$$

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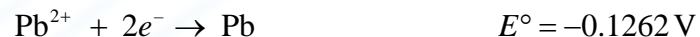
**8.19.** It might seem plausible to separate lead and gold by making use of the great difference between their standard electrode potentials (Table 8.1). In order to test this idea, one might electrolyze a solution containing  $0.0100\text{ M AuNO}_3$  and  $0.0100\text{ M Pb(NO}_3)_2$  in a well-stirred tank using platinum electrodes at low current density. As the potential difference is slowly increased from zero, which metal will be deposited first? What will be the concentration of this metal ion in solution when the second metal begins to be deposited? Do you think this is an acceptable method of separating the two metals?

**Solution:**

Given: Table 8.1,  $c_{\text{AuNO}_3} = 0.0100\text{ M}$ ,  $c_{\text{Pb(NO}_3)_2} = 0.0100\text{ M}$

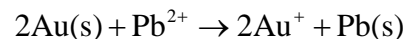
Required: see above

From Table 8.1 the two standard reduction potentials are given by,



We can see that  $\text{Au}^+$  has a much higher reduction potential than  $\text{Pb}^{2+}$ , therefore gold will be deposited first.

As the  $\text{Au}^+$  concentration falls, the lead begins to be deposited. Therefore we have,



With  $z = 2$ .

The potential for this reaction is given by,

$$E^\circ = -1.692\text{ V} - 0.1262\text{ V}$$

$$E^\circ = -1.8182\text{ V}$$

Following the procedure used in problem 8.17, we can calculate the concentration of  $\text{Au}^+$ .



$$K_c = \frac{[\text{Au}^+]^2}{[\text{Pb}^{2+}]}$$

$$E^\circ / V = \frac{0.0257}{z} \ln K^\circ$$

$$K^\circ = \exp\left(\frac{z(E^\circ / V)}{0.0257}\right)$$

$$\frac{[\text{Au}^+]^2}{[\text{Pb}^{2+}]} = \exp\left(\frac{z(E^\circ / V)}{0.0257}\right)$$

$$c_{\text{Au}^+} = \sqrt{0.0100 \text{ M} \exp\left(\frac{2(-1.8182)}{0.0257}\right)}$$

$$c_{\text{Au}^+} = 1.88\,335\,766 \times 10^{-32} \text{ M}$$

$$\boxed{c_{\text{Au}^+} = 1.88 \times 10^{-32} \text{ M}}$$

The conclusion is that only an infinitesimal amount of gold will be left in the solution by the time the lead starts to deposit at the electrode. This is shown by the negligible concentration of gold. Therefore, this is an acceptable way to separate the two metals.

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**8.20.** Calculate the emf of the cell

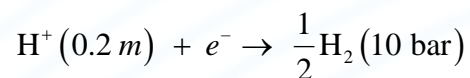


**Solution:**

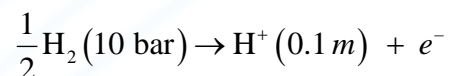
Given: see above

Required:  $E$

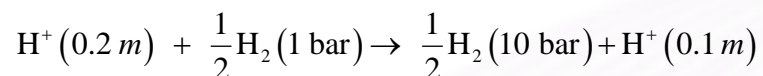
At the right-hand electrode we have the reaction:



And at the left-hand electrode we have,



The overall reaction, with  $z = 1$ , is:



To calculate the cell emf, we use Eq. 8.7,

$$E^\circ = \frac{0.0257}{z} \ln K^\circ, \text{ where } z = 1$$

$$E = 0.0257 \ln \frac{0.2 \times (1 \text{ bar})^{\frac{1}{2}}}{0.1 \times (10 \text{ bar})^{\frac{1}{2}}}$$

$$E = -0.0117743359 \text{ V}$$

$$\boxed{E = -11.8 \text{ mV}}$$

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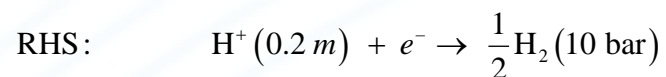
**\*8.21.** Suppose that the cell in Problem 8.20 is set up but that the two solutions are separated by a membrane that is permeable to  $\text{H}^+$  ions but impermeable to  $\text{Cl}^-$  ions. What will be the emf of the cell at  $25^\circ\text{C}$ ?

**Solution:**

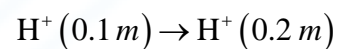
Given: Problem 8.20, a membrane that is only permeable to  $\text{H}^+$

Required:  $E$

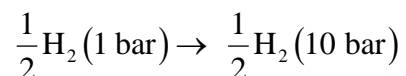
From problem 8.20, we have the half reactions at each electrode as:



Every  $\text{H}^+$  ion produced in the LHS solution will have to pass through the membrane to preserve the electrical neutrality (ion gradient).



The net reaction is therefore,



The cell emf is calculated from Eq. 8.27,

$$E = \frac{RT}{F} \ln \frac{m_2}{m_1}, \text{ where } z = 1$$

We take the ratio of pressures as a measure of the ratio of molalities.

$$E = 0.0257 \ln \frac{(1 \text{ bar})^{\frac{1}{2}}}{(10 \text{ bar})^{\frac{1}{2}}}$$

$$E = -0.029\,588\,218\,4 \text{ V}$$

$$\boxed{E = -29.6 \text{ mV}}$$

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**\*8.22.** A typical biological cell has a volume of  $10^{-9} \text{ cm}^3$ , a surface area of  $10^{-6} \text{ cm}^2$ , and a membrane thickness of  $10^{-6} \text{ cm}$ ; the dielectric constant of the membrane may be taken as 3. Suppose that the concentration of  $\text{K}^+$  ions inside the cell is  $0.155 \text{ M}$  and that the Nernst potential across the cell wall is  $0.085 \text{ V}$ .

- Calculate the net charge on either side of the wall, and
- Calculate the fraction of the  $\text{K}^+$  ions in the cell that are required to produce this charge.

**Solution:**

Given:  $V = 10^{-9} \text{ cm}^3$ ,  $A = 10^{-6} \text{ cm}^2$ ,  $l = 10^{-6} \text{ cm}$ ,  $\epsilon = 3$ ,  $c_{\text{K}^+} = 0.155 \text{ M}$ ,  $\Delta\Phi = 0.085 \text{ V}$

Required: see above

- The net charge on either side of the wall can be calculated using  $Q = CV$ .

The capacitance is given by Eq. 8.20 as,

$$C = \frac{\epsilon_0 \epsilon A}{l}$$

We solve for the net charge in the following expression,

$$Q = \frac{\epsilon_0 \epsilon A}{l} V$$

$$Q = \frac{(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(3)(10^{-10} \text{ m}^2)}{(10^{-8} \text{ m})}(0.085 \text{ V})$$

$$Q = 2.25777 \times 10^{-14} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-1} \text{ V}$$

$$Q = 2.25777 \times 10^{-14} \text{ F V}$$

where  $1 \text{ F} = 1 \text{ C V}^{-1}$

$$\boxed{Q = 2.3 \times 10^{-14} \text{ C}}$$

- The fraction of  $\text{K}^+$  ions required to produce this charge is given by

$$\frac{Q}{e} = \frac{2.25\,777 \times 10^{-14} \text{ C}}{1.602 \times 10^{-19} \text{ C}}$$

$$\frac{Q}{e} = 140\,900 \text{ ions}$$

The number of ions inside the cell is,

$$0.155 \times 10^{-12} \times 6.022 \times 10^{23} = 9.3341 \times 10^{10}$$

Therefore the fraction of ions at the surface is,

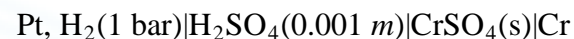
$$\frac{140\,934.4569}{9.3341 \times 10^{10}} = 1.509\,888\,012 \times 10^{-6}$$

$$\boxed{1.51 \times 10^{-6}}$$

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**\*8.23.** Calculate the emf at 25 °C of the cell



given the following standard electrode potential:



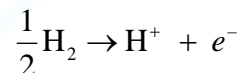
- a. First make the calculation neglecting activity coefficient corrections.
- b. Then make the calculation using activity coefficients estimated on the basis of the Debye-Hückel limiting law.

**Solution:**

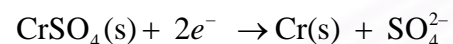
Given: see above

Required: see above

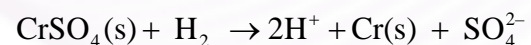
a. At the left-hand electrode we have,



and the right-hand electrode, we have,



The overall reaction is given by,



With  $E^\circ = -0.40 \text{ V}$  and  $z = 2$

The emf, neglecting the activity coefficients, is given by Eq. 8.13

$$E = E^\circ - \frac{RT}{zF} \ln \left( \frac{\cdots [Y]^y [Z]^z}{[A]^a [B]^b \cdots} \right)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln \left( [H^+]^2 [SO_4^{2-}] \right)^u$$

$$E = -0.40 \text{ V} - \frac{0.0257}{2} \ln \left( (0.002)^2 (0.001) \right)$$

$$E = -0.151\,519\,916\,5 \text{ V}$$

$$\boxed{E = -0.152 \text{ V}}$$

b. To calculate the activity coefficients, we first calculate the ionic strength of the solution from Eq. 7.103,

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I = \frac{1}{2} (1^2 \times 0.002 + 2^2 \times 0.001)$$

$$I = 0.003 \text{ M}$$

Now we rearrange the Debye-Hückel limiting law given by Eq. 7.111,

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}$$

$$\gamma_{\pm} = 10^{-0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}}$$

$$\gamma_{\pm} = 10^{-0.51(2 \times 1) \sqrt{0.003}}$$

$$\gamma_{\pm} = 0.879\,290\,334\,3$$

Substituting back into the expression for the emf obtained above we can solve for the true emf of the solution.



$$E = E^\circ - \frac{RT}{2F} \ln \left( [\text{H}^+]^2 \gamma_{\pm}^2 [\text{SO}_4^{2-}] \gamma_{\pm} \right)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln \left( [\text{H}^+]^2 [\text{SO}_4^{2-}] \gamma_{\pm}^3 \right)^u$$

$$E = -0.40 \text{ V} - \frac{0.0257}{2} \ln \left( (0.002)^2 (0.001) (0.879\,290\,334\,3)^3 \right)$$

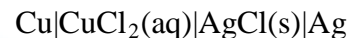
$$E = -0.146\,560\,839\,3 \text{ V}$$

$$\boxed{E = -0.147 \text{ V}}$$

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**\*8.24.** Write the individual electrode reactions and the overall reaction for



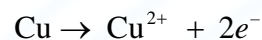
If the emf of the cell is 0.191 V when the concentration of  $\text{CuCl}_2$  is  $1.0 \times 10^{-4} M$  and is  $-0.074 V$  when the concentration is  $0.20 M$ , make an estimate of the mean activity coefficient in the latter solution.

**Solution:**

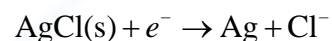
Given:  $E_1 = 0.191 V$ ,  $c_1 = 1.0 \times 10^{-4} M$ ,  $E_2 = 0.074 V$ ,  $c_2 = 0.20 M$

Required:  $\gamma_{\pm}$

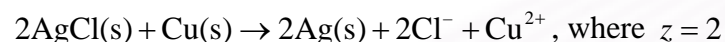
At the left-hand electrode we have,



and the right-hand electrode, we have,



The overall reaction is given by,



To a good approximation, it can be assumed that the activity coefficients at  $10^{-4} M$  are unity. (The DHLL gives  $\gamma_{\pm} = 0.988$ ) Thus the standard electrical potential is obtained by rearranging Eq. 8.13

$$E = E^{\circ} - \frac{RT}{zF} \ln \left( \frac{\cdots [\text{Y}]^y [\text{Z}]^z}{[\text{A}]^a [\text{B}]^b \cdots} \right)^u$$

$$E^{\circ} = E + \frac{RT}{2F} \ln \left( [\text{Cu}^{2+}] [\text{Cl}^{-}]^2 \right)^u$$

$$E^{\circ} = 0.191 V + \frac{0.0257}{2} \ln \left( (10^{-4}) (2 \times 10^{-4})^2 \right)$$

$$E^{\circ} = -0.146\,244\,738\,8\,V$$

Suppose that at 0.20 *M* the activity coefficients are  $\gamma_+$  and  $\gamma_-$ , then we can solve for the mean activity coefficient from Eq. 8.40.

$$E = E^\circ - \frac{RT}{2F} \ln(a_{\text{Cu}^{2+}} a_{\text{Cl}^-}^2)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln(\gamma_+ [\text{Cu}^{2+}] \gamma_-^2 [\text{Cl}^-]^2)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln([\text{Cu}^{2+}] [\text{Cl}^-]^2 \gamma_\pm^3)$$

$$-0.074 \text{ V} = -0.1462447388 \text{ V} - \frac{0.0257}{2} \ln((0.20)(0.40)^2) - \frac{0.0257}{2} \ln \gamma_\pm^3$$

$$0.0280147899 = -\frac{0.0257}{2} \ln \gamma_\pm^3$$

$$\ln \gamma_\pm^3 = -2.180139285$$

$$\gamma_\pm = 0.4834955852$$

$$\boxed{\gamma_\pm = 0.48}$$

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**\*8.25. a.** Write both electrode reactions and the overall reaction for the cell



**b.** Calculate  $E$  and  $E^\circ$  for this cell at  $25^\circ\text{C}$  from the following information:



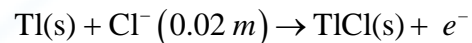
The solubility product for  $\text{TlCl}$  is  $1.6 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}$  at  $25^\circ\text{C}$ .

**Solution:**

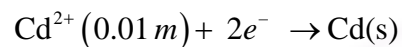
Given: cell above,  $K_{\text{sp}} = 1.6 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}$ ,  $T = 25^\circ\text{C}$

Required: see above

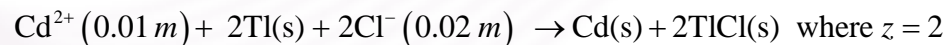
a. The left-hand or anode reaction is:



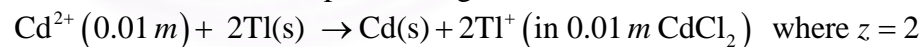
The right-hand, or cathode reaction is:



The overall reaction is:



b. To use the electrical potentials given above, we rewrite the overall equation as ( $\text{Cl}^-$  is a spectator ion):



The standard electrical potential is given by,

$$E^\circ = -0.40\text{ V} - (-0.34\text{ V})$$

$$\boxed{E^\circ = -0.06\text{ V}}$$

To solve for the emf, we use Eq. 8.13,

$$E = E^\circ - \frac{RT}{2F} \ln \left( \frac{[\text{Ti}^+]^2}{[\text{Cd}^{2+}]} \right)^u$$

$$\text{where } K_{\text{sp}} = [\text{Ti}^+][\text{Cl}^-]$$

$$[\text{Ti}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]}$$

$$E = E^\circ - \frac{0.0257}{2} \ln \left( \frac{K_{\text{sp}}^2}{[\text{Cl}^-]^2 [\text{Cd}^{2+}]} \right)^u$$

$$E = -0.06 \text{ V} - \frac{0.0257}{2} \ln \left( \frac{(1.6 \times 10^{-3})^2}{(0.02)^2 (0.01)} \right)^u$$

$$E = -0.054 \text{ 265 210 7 V}$$

$$\boxed{E = -0.054 \text{ V}}$$

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**8.26.** Problem 7.44 involved calculating the concentrations on each side of a membrane after a Donnan equilibrium had become established. Which side of the membrane is positively charged? Calculate the Nernst potential across the membrane if the temperature is 37 °C.

**Solution:**

Given: Problem 7.44,  $T = 37\text{ °C}$

Required:  $\Delta\Phi$  (used for concentration cells)

We follow the same procedure as problem 8.18 to solve for the Nernst potential.

From problem 7.44, we have the equilibrium concentrations of potassium and chloride as,

right-hand side	left-hand side
$[K^+] = 0.04\text{ M}$	$[K^+] = 0.16\text{ M}$
$[Cl^-] = 0.04\text{ M}$	$[Cl^-] = 0.01\text{ M}$

The diffusible  $K^+$  ions are at a higher potential on the right-hand side of the membrane; there is thus a tendency for few of them to cross to the left-hand side and create a positive potential there. The same conclusion can be made by considering the diffusible  $Cl^-$  ions; they are at a higher potential on the left-hand side, and few tend to cross to the right-hand side and create a negative potential.

The Nernst potential is given by Eq. 8.19 as,

$$\Delta\Phi = \frac{RT}{zF} \ln \frac{c_1}{c_2}$$

$$\Delta\Phi = \frac{8.3145\text{ J K}^{-1}\text{ mol}^{-1} \times 310.15\text{ K}}{1 \times 96485\text{ C mol}^{-1}} \ln \frac{0.16\text{ M}}{0.04\text{ M}}$$

$$\Delta\Phi = 0.037\,051\,310\,9\text{ J C}^{-1}$$

where  $1\text{ J} = 1\text{ C V}$

$$\boxed{\Delta\Phi = 37\text{ mV}}$$

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**8.27.** The oxidation of lactate to pyruvate by the oxidized form of cytochrome *c*—represented as cytochrome *c* ( $\text{Fe}^{3+}$ )—is an important biological reaction. The following are the relevant  $E^{\circ'}$  values, relating to pH 7 and 25 °C:

	$E^{\circ'}/\text{V}$
pyruvate $^- + 2\text{H}^+ + 2e^- \rightarrow$ lactate $^-$	-0.185
cytochrome <i>c</i> ( $\text{Fe}^{3+}$ ) + $e^- \rightarrow$ cytochrome <i>c</i> ( $\text{Fe}^{2+}$ )	0.254

Calculate the equilibrium ratio

$$\frac{[\text{cytochrome } c (\text{Fe}^{2+})]^2 [\text{pyruvate}^-] [\text{H}^+]^2}{[\text{cytochrome } c (\text{Fe}^{3+})]^2 [\text{lactate}^-]}$$

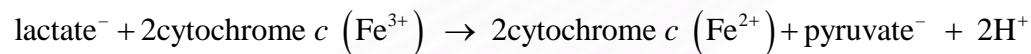
at pH 7 and 25 °C. Also calculate the ratio at pH 6.

**Solution:**

Given: pH = 7,  $T = 25\text{ °C}$

Required: equilibrium ratio at pH 7 and pH 6

We begin by first writing the overall reaction as:



Where  $z = 2$  and

$$E^{\circ'} = 0.254\text{ V} + 0.185\text{ V}$$

$$E^{\circ'} = 0.439\text{ V}$$

If  $K'$  is the equilibrium constant given at pH 7, then

$$K' = \frac{[\text{cytochrome } c (\text{Fe}^{2+})]^2 [\text{pyruvate}^-] [\text{H}^+]^2}{[\text{cytochrome } c (\text{Fe}^{3+})]^2 [\text{lactate}^-]}$$

And the equilibrium ratio at pH 7 is just  $K'$  (unitless).

From Eq. 8.6 we can obtain  $K'$ ,

$$E^{\circ} = \frac{RT}{zF} \ln K^{\circ}$$

$$E^{\circ'} = \frac{0.0257}{2} \ln K'$$

$$K' = \exp\left(\frac{2}{0.0257} E^{\circ'}\right)$$

$$K' = \exp\left(\frac{2}{0.0257} (0.439)\right)$$

$$K' = 6.870\,472\,098 \times 10^{14}$$

$$\boxed{K' = 6.87 \times 10^{14}}$$

At pH 6, the equilibrium ratio is  $K''$

$$K_{\text{true}} = K' [\text{H}^+]^2 = \frac{[\text{cytochrome } c (\text{Fe}^{2+})]^2 [\text{pyruvate}^-]}{[\text{cytochrome } c (\text{Fe}^{3+})]^2 [\text{lactate}^-]}$$

$$K_{\text{true}} = K' (10^{-7} \text{ M})^2 = K'' (10^{-6} \text{ M})^2$$

$$K'' = 6.870\,472\,098 \times 10^{14} \times \frac{(10^{-7} \text{ M})^2}{(10^{-6} \text{ M})^2}$$

$$K'' = 6.870\,472\,098 \times 10^{12}$$

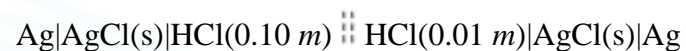
$$\boxed{K'' = 6.87 \times 10^{12}}$$

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8.28. Suppose that the cell



is set up and that the membrane separating the two solutions is permeable only to  $\text{H}^+$  ions. What is the emf of the cell at  $25\text{ }^\circ\text{C}$ ?

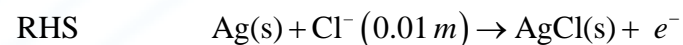
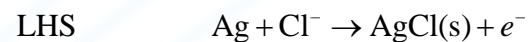
**Solution:**

Given: see above, a membrane that is only permeable to  $\text{H}^+$

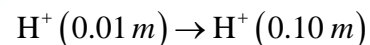
Required:  $E$

We can solve this problem in a similar manner as problem 8.21.

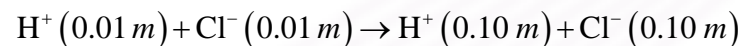
The half reactions for each electrode are:



The electrical neutrality is maintained by the passage of  $\text{H}^+$  ions from right to left:



The net reaction is therefore,



The cell emf is calculated from Eq. 8.13,

$$E = E^\circ - \frac{0.0257}{z} \ln K^\circ, \text{ where } z = 1 \text{ and } E^\circ = 0$$

$$K^\circ = \frac{[\text{H}^+_{\text{prod}}][\text{Cl}^-_{\text{prod}}]}{[\text{H}^+_{\text{react}}][\text{Cl}^-_{\text{react}}]}$$

$$E = -0.0257 \ln \frac{(0.10 \text{ M})(0.10 \text{ M})}{(0.01 \text{ M})(0.01 \text{ M})}$$

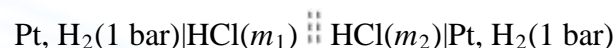
$$E = -0.1183528738 \text{ V}$$

$$\boxed{E = -0.12 \text{ V}}$$

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8.29. a. Consider the cell



in which the solutions are separated by a partition that is permeable to both  $\text{H}^+$  and  $\text{Cl}^-$ . The ratio of the speeds with which these ions pass through the membrane is the ratio of their transport numbers  $t_+$  and  $t_-$ . Derive an expression for the emf of this cell.

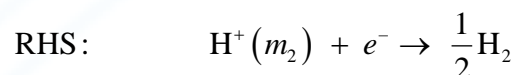
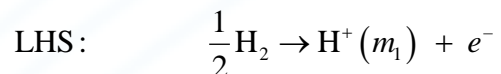
b. If when  $m_1 = 0.01 \text{ m}$  and  $m_2 = 0.01 \text{ m}$  the emf is 0.0190 V, what are the transport numbers of the  $\text{H}^+$  and  $\text{Cl}^-$  ions?

**Solution:**

Given: see above

Required: see above

a. The half reactions for each electrode are:



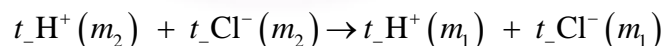
To maintain electrical neutrality of the solutions, for every mole of  $\text{H}^+$  produced in the LHS solution,  $t_+$  mol of  $\text{H}^+$  will cross the membrane from the left to the right, and  $t_-$  mol of  $\text{Cl}^-$  ions will pass from right to left. In the LHS solution, there is therefore a net gain of,

$$(1 - t_+) \text{ mol} = t_- \text{ mol of } \text{H}^+ \text{ and of } t_- \text{ mol of } \text{Cl}^-.$$

In the RHS solution, the net loss is

$$(1 - t_+) \text{ mol} = t_- \text{ mol of } \text{H}^+ \text{ and of } t_- \text{ mol of } \text{Cl}^-$$

The overall process is thus,



The emf is given by Eq. 8.13,

$$E = E^\circ - \frac{0.0257}{z} \ln K^\circ, \text{ where } z = 1 \text{ and } E^\circ = 0$$

$$E = -0.0257 \ln \frac{m_1^+ m_1^-}{m_2^+ m_2^-}$$

$$E = 0.0257 \ln \left( \frac{m_2^+}{m_1^+} \right)^2$$

$$E = 0.0257 \times 2t_- \ln \frac{m_2}{m_1}$$

b. To calculate the transport numbers we use the expression derived above with  $m_1 = 0.01 \text{ m}$ ,  $m_2 = 0.10 \text{ m}$

$$E = 0.0257 \times 2t_- \ln \frac{m_2}{m_1}$$

$$t_- = \frac{0.0190 \text{ V}}{0.0257 \times 2} \div \ln \frac{0.10 \cancel{\text{m}}}{0.01 \cancel{\text{m}}}$$

$$t_- = 0.160\,536\,870\,7$$

$$t_- = 0.161$$

$$t_+ = 1 - 0.160\,536\,870\,7$$

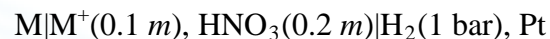
$$t_+ = 0.839\,463\,129\,3$$

$$t_+ = 0.839$$

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**8.30.** The metal M forms a soluble nitrate and a very slightly soluble chloride. The cell



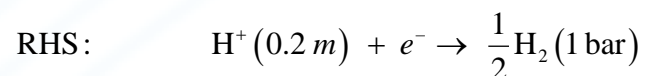
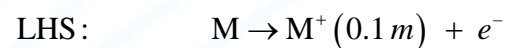
has a measured  $E = -0.40\text{ V}$  at  $298.15\text{ K}$ . When sufficient solid KCl is added to make the solution of the cell  $0.20\text{ }m$  in  $\text{K}^+$ , the emf changes to  $-0.15\text{ V}$  at  $298.15\text{ K}$  as MCl precipitates. Calculate the  $K_{\text{sp}}$  of MCl, taking all activity coefficients to be unity.

**Solution:**

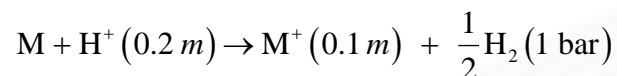
Given:  $E_1 = -0.40\text{ V}$ ,  $T = 298.15\text{ K}$ ,  $c_{\text{K}^+} = 0.20\text{ }m$ ,  $E_2 = -0.15\text{ V}$ ,  $\gamma_{\pm} = 1$

Required:  $K_{\text{sp}}$

The half reactions for each electrode are:



The overall reaction is given by,



with  $z = 1$  and

$$E^{\circ} = E_{\text{H}^+|\text{H}_2}^{\circ} - E_{\text{M}^+|\text{M}}^{\circ}$$

$$. E^{\circ} = 0 - E_{\text{M}^+|\text{M}}^{\circ}$$

$$E^{\circ} = -E_{\text{M}^+|\text{M}}^{\circ}$$

Using Eq. 8.13,

$$E = E^\circ - \frac{RT}{zF} \ln \left( \frac{\cdots [Y]^y [Z]^z}{[A]^a [B]^b \cdots} \right)^u, \text{ where } z = 1$$

$$E^\circ = E + \frac{RT}{zF} \ln \left( \frac{[M^+]\gamma_{M^+}}{[H^+]\gamma_{H^+}} \right)$$

$$E^\circ_{M^+|M} = -0.40 \text{ V} + 0.0257 \ln \frac{0.1 \cancel{m}}{0.2 \cancel{m}}$$

$$E^\circ_{M^+|M} = -0.4178138825 \text{ V}$$

Upon addition of KCl, almost all of the  $M^+$  precipitates, and  $0.10 \text{ m Cl}^-$  is in excess. The value of  $M^+$  in solution is found from the  $K_{sp}$ ,

$$K_{sp} = [M^+][Cl^-]$$

$$[M^+] = \frac{K_{sp}}{[Cl^-]}$$

Using the Nernst equation, we can solve for the solubility product,

$$E = E^\circ - \frac{RT}{zF} \ln \left( \frac{K_{sp}}{[H^+][Cl^-]} \right)$$

$$\frac{E - E^\circ}{-0.0257} = \ln \left( \frac{K_{sp}}{[H^+][Cl^-]} \right)$$

$$K_{sp} = [H^+][Cl^-] \exp \left( \frac{E - E^\circ}{-0.0257} \right)$$

$$K_{sp} = (0.20 \text{ m})(0.10 \text{ m}) \exp \left( \frac{-0.15 \text{ V} - (-0.4178138825 \text{ V})}{-0.0257} \right)$$

$$K_{sp} = 5.961362163 \times 10^{-7} \text{ m}^2$$

$$\boxed{K_{sp} = 6.0 \times 10^{-7} \text{ m}^2}$$

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- 8.31.** The substance nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) plays an important role in biological systems; under the action of certain enzymes it can react with a reducing agent and release a proton to the solution to form its reduced form NADH. With pyruvate the reduced form NADH undergoes the reaction



The appropriate  $E^\circ'$  values, relating to 25 °C and pH 7, are



Use these values to calculate  $\Delta G^\circ'$  for the reaction, and also the equilibrium ratio

$$\frac{[\text{lactate}^-][\text{NAD}^+]}{[\text{pyruvate}^-][\text{NADH}][\text{H}^+]}$$

(a) at pH 7, and (b) at pH 8.

**Solution:**

Given: see above

Required:  $\Delta G^\circ'$ , equilibrium ratio

- a. The overall reaction that is obtained by reversing the second half reaction and summing the two together:



$$E^\circ' = -0.19 \text{ V} - (-0.34 \text{ V})$$

$$E^\circ' = 0.15 \text{ V}$$

To find  $\Delta G^\circ'$  we use Eq. 8.2,

$$\Delta G^\circ = -zFE^\circ$$

$$\Delta G^{\circ'} = -2 \times 96\,485 \text{ C mol}^{-1} \times 0.15 \text{ V}$$

$$\Delta G^{\circ'} = -28\,945.5 \text{ C V mol}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\Delta G^{\circ'} = -28\,945.5 \text{ J mol}^{-1}$$

$$\boxed{\Delta G^{\circ'} = -29 \text{ kJ mol}^{-1}}$$

To solve for the equilibrium ratio, we follow the thought process used in problem 8. 27. If  $K'$  is the equilibrium constant given at pH 7, then

$$K' = \frac{[\text{lactate}^-][\text{NAD}^+]}{[\text{pyruvate}^-][\text{NADH}][\text{H}^+]}$$

And the equilibrium ratio at pH 7 is just  $K'$  (unitless)

From Eq. 8.5, we can solve for  $K'$ .

$$\Delta G^{\circ'} = -RT \ln K'$$

$$K' = \exp\left(\frac{\Delta G^{\circ'}}{-RT}\right)$$

$$K' = \exp\left(\frac{-28945.5 \text{ J mol}^{-1}}{(-8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right)$$

$$K' = 117\,763.1471 \text{ dm}^3 \text{ mol}^{-1}$$

$$\boxed{K' = 1.2 \times 10^5}$$

b. At pH 8, the equilibrium ratio is  $K''$



$$K_{\text{true}} = K'[\text{H}^+] = \frac{[\text{lactate}^-][\text{NAD}^-]}{[\text{pyruvate}^-][\text{NADH}]}$$

$$K_{\text{true}} = K'(10^{-7} \text{ M}) = K''(10^{-8} \text{ M})$$

$$K'' = 117\,763.1471 \times \frac{(10^{-7} \text{ M})}{(10^{-8} \text{ M})}$$

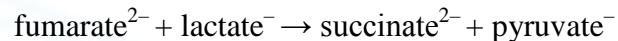
$$K'' = 1177\,631.471$$

$$\boxed{K'' = 1.2 \times 10^6}$$

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**8.32. a.** Calculate the standard emf  $E^\circ$  for the reaction



on the basis of the following information:



The  $E^{\circ'}$  values relate to pH 7. The temperature coefficient  $\partial E/\partial T$  for this cell is  $2.18 \times 10^{-5} \text{ V K}^{-1}$ .

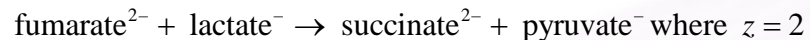
**b.** Calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 25 °C.

**Solution:**

Given: pH 7,  $\partial E/\partial T = 2.18 \times 10^{-5} \text{ V K}^{-1}$

Required: see above

a. To find the standard emf, we first determine that the overall reaction is:



Therefore,

$$E^{\circ'} = 0.031 \text{ V} - (-0.185 \text{ V})$$

$$\boxed{E^{\circ'} = E^\circ = 0.216 \text{ V}}$$

(Note that this is also  $E^\circ$ , the hydrogen ions having cancelled out.)

b. To calculate  $\Delta G^\circ$ , we use  $E^\circ$  from above and substitute into Eq. 8.2

$$\Delta G^\circ = -zFE^\circ$$

$$\Delta G^\circ = -2 \times 96\,485 \text{ C mol}^{-1} \times 0.216 \text{ V}$$

$$\Delta G^\circ = -41\,681.52 \text{ C V mol}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\boxed{\Delta G^\circ = -41.7 \text{ kJ mol}^{-1}}$$

The entropy change is obtained from Eq 8.23,

$$\Delta S = zF \left( \frac{\partial E}{\partial T} \right)_P$$

$$\Delta S = 2 \times 96\,485 \text{ C mol}^{-1} \times 2.18 \times 10^{-5} \text{ V K}^{-1}$$

$$\Delta S = 4.206\,746 \text{ C V mol}^{-1} \text{ K}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\boxed{\Delta S = 4.21 \text{ J mol}^{-1} \text{ K}^{-1}}$$

To calculate enthalpy, we use the relationship between Gibbs energy and entropy we learned earlier as,

$$\Delta H = \Delta G + T \Delta S$$

$$\Delta H = -41\,681.52 \text{ J mol}^{-1} + (298.15 \text{ K}) (4.206\,746 \text{ J mol}^{-1} \text{ K}^{-1})$$

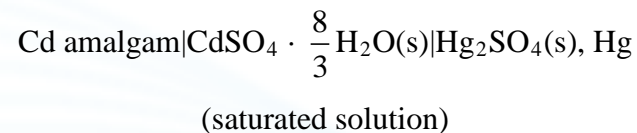
$$\Delta H = -40\,427.278\,68 \text{ J mol}^{-1}$$

$$\boxed{\Delta H = -40.4 \text{ kJ mol}^{-1}}$$

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**8.33.** The Weston standard cell (see Figure 8.2b) is



**a.** Write the cell reaction.

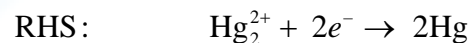
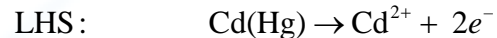
**b.** At 25 °C, the emf is 1.018 32 V and  $\partial E^\circ / \partial T = -5.00 \times 10^{-5} \text{ V K}^{-1}$ . Calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ .

**Solution:**

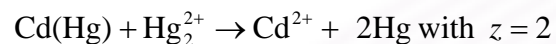
Given:  $T = 25^\circ\text{C}$ ,  $E^\circ = 1.018\,32 \text{ V}$ ,  $\partial E / \partial T = 5.00 \times 10^{-5} \text{ V K}^{-1}$

Required: see above

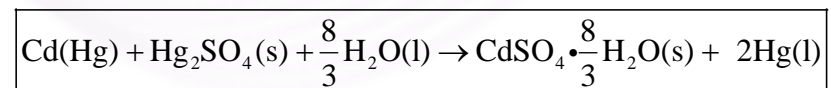
**a.** The half reactions for each electrode are:



The overall reaction is given by,



Since the solution is saturated with  $\text{Hg}_2\text{SO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ , the overall reaction can be written as,



**b.** We can calculate  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  in a similar manner shown in problem 8.32.  
From Eq. 8.2,

$$\Delta G^\circ = -zFE^\circ$$

$$\Delta G^\circ = -2 \times 96\,845 \text{ C mol}^{-1} \times 1.018\,32 \text{ V}$$

$$\Delta G^\circ = -196\,505.210\,4 \text{ C V mol}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\boxed{\Delta G^\circ = -196.5 \text{ kJ mol}^{-1}}$$

The entropy change is obtained from Eq 8.23,

$$\Delta S = zF \left( \frac{\partial E}{\partial T} \right)_P$$

$$\Delta S = 2 \times 96\,845 \text{ C mol}^{-1} \times 5.00 \times 10^{-5} \text{ V K}^{-1}$$

$$\Delta S = 9.6485 \text{ C V mol}^{-1} \text{ K}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\boxed{\Delta S = 9.65 \text{ J mol}^{-1} \text{ K}^{-1}}$$

$$\Delta H = \Delta G + T\Delta S$$

$$\Delta H = -196\,505.2104 \text{ J mol}^{-1} + (298.15 \text{ K})(9.6485 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$\Delta H = -199\,381.9107 \text{ J mol}^{-1}$$

$$\boxed{\Delta H = -199 \text{ kJ mol}^{-1}}$$

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**8.34.** Salstrom and Hildebrand [*J. Amer. Chem. Soc.*, 52, 4650(1930)] reported the following data for the cell

	Ag(s) AgBr(s) HBr(aq) Br <sub>2</sub> (g, 1 atm) Pt					
$t/^{\circ}\text{C}$	442.3	456.0	490.9	521.4	538.3	556.2
$E/\text{V}$	0.8031	0.7989	0.7887	0.7803	0.7751	0.7702

Find the temperature coefficient for this cell assuming a linear dependence of the cell potential with temperature. What is the entropy change for the cell reaction?

**Solution:**

Given: data above

Required:  $\Delta S$

To solve for  $\Delta S$ , we need to find the temperature coefficient,  $\left(\frac{\partial E}{\partial T}\right)_p$  from the data above.

Since we are only interested in the slope of the line best fit, we do not need to convert the temperature data to Kelvin.

We can perform a linear regression analysis, using  $t$  as the independent variable and  $E$  as the dependent variable.

The result is:

$$E = 0.930\,463\,55 - 2.883\,37 \times 10^{-4} t$$

Differentiation with respect to  $t$  gives,

$$\left(\frac{\partial E}{\partial T}\right)_p = -2.883\,37 \times 10^{-4} \text{ V }^{\circ}\text{C}^{-1}$$

$$\left(\frac{\partial E}{\partial T}\right)_p = -2.883\,37 \times 10^{-4} \text{ V K}^{-1}$$

Substituting this value into Eq. 8.23 gives the entropy change,

$$\Delta S = zF \left( \frac{\partial E}{\partial T} \right)_P$$

$$\Delta S = 96\,485 \text{ C mol}^{-1} \times -2.883\,37 \times 10^{-4} \text{ V K}^{-1}$$

$$\Delta S = -27.820\,195\,45 \text{ C V K}^{-1} \text{ mol}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\boxed{\Delta S = -27.82 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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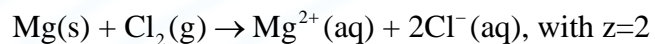
**8.35.** The reaction taking place in the cell  $\text{Mg(s)}|\text{Mg}^{2+}(\text{aq}), \text{Cl}^{-}(\text{aq})|\text{Cl}_2(\text{g}, 1 \text{ atm})|\text{Pt}$  is found to have an entropy change of  $-337.3 \text{ J K}^{-1} \text{ mol}^{-1}$  under standard conditions. What is the temperature coefficient for the cell?

**Solution:**

Given:  $\Delta S^{\circ} = -337.3 \text{ J K}^{-1} \text{ mol}^{-1}$

Required:  $\left(\frac{\partial E}{\partial T}\right)_p$

The overall reaction we are concerned with is,



Rearranging Eq. 8.23, we can solve for the temperature coefficient,

$$\Delta S = zF \left(\frac{\partial E}{\partial T}\right)_p$$

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S}{zF}$$

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{-337.3 \text{ J K}^{-1} \cancel{\text{mol}^{-1}}}{2 \times 96485 \text{ C } \cancel{\text{mol}^{-1}}}$$

$$\left(\frac{\partial E}{\partial T}\right)_p = -1.7479401 \times 10^{-3} \text{ J C}^{-1} \text{ K}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\boxed{\left(\frac{\partial E}{\partial T}\right)_p = -1.748 \times 10^{-3} \text{ V K}^{-1}}$$

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**\*8.36. a.** Estimate the Gibbs energy of formation of the fumarate ion, using data in Problem 8.32 and the following values.

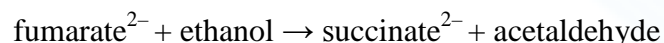
$$\Delta_f G^\circ (\text{succinate, aq}) = -690.44 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ (\text{acetaldehyde, aq}) = 139.08 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ (\text{ethanol, aq}) = -181.75 \text{ kJ mol}^{-1}$$

$$\text{acetaldehyde} + 2\text{H}^+ + 2e^- \rightarrow \text{ethanol} \quad E^\circ = -0.197 \text{ V}$$

**b.** If the  $\partial E^\circ / \partial T$  value for the process



is  $2.18 \times 10^{-5} \text{ V K}^{-1}$ , estimate the enthalpy of formation of the fumarate ion from the following values.

$$\Delta_f H^\circ (\text{succinate, aq}) = -908.68 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{acetaldehyde, aq}) = -210.66 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{ethanol, aq}) = -287.02 \text{ kJ mol}^{-1}$$

**Solution:**

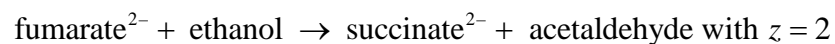
$$\text{Given: problem 8.32, } \Delta_f G^\circ, \left( \frac{\partial E}{\partial T} \right)_P = 2.18 \times 10^{-5} \text{ V K}^{-1}, \Delta_f H^\circ$$

Required: see above

a. The two reactions of interest are,



Subtracting (2) from (1) gives the desired reaction:



And a standard electrical potential of,

$$E^{\circ'} = 0.031 \text{ V} + 0.197 \text{ V}$$

$$E^{\circ'} = 0.228 \text{ V}$$

The Gibbs energy for the reaction is calculated from Eq. 8.2

$$\Delta G^{\circ} = -zFE^{\circ}$$

$$\Delta G^{\circ} = -2 \times 96\,845 \text{ C mol}^{-1} \times 0.228 \text{ V}$$

$$\Delta G^{\circ} = -43\,997.16 \text{ C V mol}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\Delta G^{\circ} = -43\,997.16 \text{ J mol}^{-1}$$

To find the Gibbs energy of formation of fumarate, we use Eq. 3.91

$$\Delta G^{\circ} = \sum \Delta_f G^{\circ}(\text{products}) - \sum \Delta_f G^{\circ}(\text{reactants})$$

$$\Delta G^{\circ} = \Delta_f G^{\circ}_{\text{succinate}} + \Delta_f G^{\circ}_{\text{acetaldehyde}} - (\Delta_f G^{\circ}_{\text{ethanol}} + \Delta_f G^{\circ}_{\text{fumarate}})$$

$$\Delta_f G^{\circ}_{\text{fumarate}} = \Delta_f G^{\circ}_{\text{succinate}} + \Delta_f G^{\circ}_{\text{acetaldehyde}} - \Delta_f G^{\circ}_{\text{ethanol}} - \Delta G^{\circ}$$

$$\Delta_f G^{\circ}_{\text{fumarate}} = -690.44 \text{ kJ mol}^{-1} + 139.08 \text{ kJ mol}^{-1} - (-181.74 \text{ kJ mol}^{-1}) - (-43.99716 \text{ kJ mol}^{-1})$$

$$\Delta_f G^{\circ}_{\text{fumarate}} = -325.61284 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_f G^{\circ}_{\text{fumarate}} = -326 \text{ kJ mol}^{-1}}$$

b. To find the enthalpy of formation of fumarate, we first need to find the enthalpy of the reaction. From Eq. 8.23, we calculate the entropy, and then use it to find the enthalpy.

$$\Delta S = zF \left( \frac{\partial E}{\partial T} \right)_p$$

$$\Delta S = 2 \times 96\,485 \text{ C mol}^{-1} \times (2.18 \times 10^{-5} \text{ V K}^{-1})$$

$$\Delta S = -4.222\,442 \text{ C V mol}^{-1} \text{ K}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\Delta S = -4.222\,442 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = \Delta G + T\Delta S$$

$$\Delta H = -43\,997.16 + (298.15)(-4.222\,442)$$

$$\Delta H = -45\,256.08 \text{ J mol}^{-1}$$

$$\Delta H = -45.25\,608 \text{ kJ mol}^{-1}$$

To find the enthalpy of formation of fumarate, we use Eq. 2.53

$$\Delta H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

$$\Delta H^\circ = \Delta_f H^\circ_{\text{succinate}} + \Delta_f H^\circ_{\text{acetaldehyde}} - (\Delta_f H^\circ_{\text{ethanol}} + \Delta_f H^\circ_{\text{fumarate}})$$

$$\Delta_f H^\circ_{\text{fumarate}} = \Delta_f H^\circ_{\text{succinate}} + \Delta_f H^\circ_{\text{acetaldehyde}} - \Delta_f H^\circ_{\text{ethanol}} - \Delta H^\circ$$

$$\Delta_f H^\circ_{\text{fumarate}} = -908.68 \text{ kJ mol}^{-1} - 210.66 \text{ kJ mol}^{-1} - (-287.02 \text{ kJ mol}^{-1}) - (-45.25\,608 \text{ kJ mol}^{-1})$$

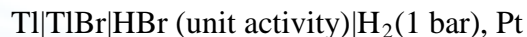
$$\Delta_f H^\circ_{\text{fumarate}} = -787.06\,392 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta_f H^\circ_{\text{fumarate}} = -787 \text{ kJ mol}^{-1}}$$

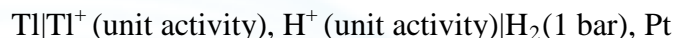
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**\*8.37. a.** Calculate the emf at 298.15 K for the cell



**b.** Calculate  $\Delta H$  for the cell reaction in the following cell.



For the half-cell

$$\text{Tl}^+ + e^- \rightarrow \text{Tl} \quad E^\circ = 0.34 \text{ V}$$

$$\partial E / \partial T = -0.003 \text{ V/K and}$$

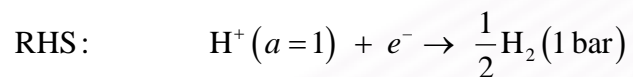
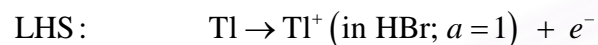
$$K_{\text{sp}}(\text{TlBr}) = 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$$

**Solution:**

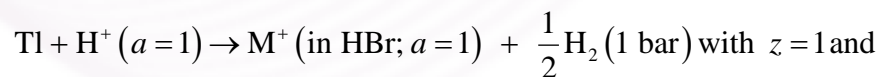
Given:  $T = 298.15 \text{ K}$ ,  $E^\circ = 0.34 \text{ V}$ ,  $\partial E / \partial T = -0.003 \text{ V K}^{-1}$ ,  $K_{\text{sp}}(\text{TlBr}) = 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$

Required: see above,

a. The half reactions for each electrode are:



The overall reaction is given by,



$$E^\circ = E_{\text{H}^+|\text{H}_2}^\circ - E_{\text{Tl}^+|\text{Tl}}^\circ$$

$$E^\circ = 0 - E_{\text{Tl}^+|\text{Tl}}^\circ$$

$$E^\circ = -E_{\text{Tl}^+|\text{Tl}}^\circ = -0.34 \text{ V}$$

The emf is given by Eq. 8.13,

$$E = E^\circ - 0.0257 \ln \left( \frac{[\text{Tl}^+]}{[\text{H}^+]} \right)^u$$

$$K_{\text{sp}} = [\text{Tl}^+][\text{Br}^-]$$

$$[\text{Tl}^+] = \frac{K_{\text{sp}}}{[\text{Br}^-]}$$

$$E = E^\circ - 0.0257 \ln \left( \frac{K_{\text{sp}}}{[\text{Br}^-][\text{H}^+]} \right)^u$$

$$E = -0.34 - 0.0257 \ln \left( \frac{10^{-4} \text{ mol}^{-2} \text{ dm}^{-6}}{1 \times 1} \right)^u$$

$$E = -0.103 \text{ 294 252 V}$$

$$\boxed{E = -0.10 \text{ V}}$$

$$\boxed{E = 0.0257 \times 2 \ln \frac{m_2}{m_1}}$$

b. We can calculate the enthalpy using Eq. 8.25 and the data given for the half cell reaction.

$$\Delta H = -zF \left( E - T \frac{\partial E}{\partial T} \right)$$

$$\Delta H = -1 \times 96\,485 \text{ C mol}^{-1} \left( -0.34 \text{ V} - (298.25 \text{ K}) (-0.003 \text{ V K}^{-1}) \right)$$

$$\Delta H = 53\,496.10825 \text{ C V mol}^{-1}$$

where  $1 \text{ J} = 1 \text{ C V}$

$$\Delta H = 53\,496.10825 \text{ J mol}^{-1}$$

$$\boxed{\Delta H = 535 \text{ kJ mol}^{-1}}$$

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**8.38.** Calculate the solubility product and the solubility of AgBr at 25 °C on the basis of the following standard electrode potentials:

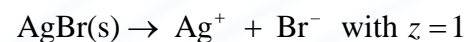


**Solution:**

Given:  $T = 25^\circ\text{C}$

Required:  $K_{sp}$ ,  $s$

The desired reaction is obtained by subtracting the second reaction from the first.



$$E^\circ = 0.0713 \text{ V} - 0.7996 \text{ V}$$

$$E^\circ = -0.7283 \text{ V}$$

We can calculate the solubility product from Eq. 8.13,

$$E^\circ = 0.0257 \ln \left( [\text{Ag}^+] [\text{Br}^-] \right)^u$$

$$K_{sp} = [\text{Ag}^+] [\text{Br}^-]$$

$$E^\circ = 0.0257 \ln K_{sp}$$

$$K_{sp} = \exp \left( \frac{E^\circ}{0.0257} \right)$$

$$K_{sp} = \exp \left( \frac{-0.7283}{0.0257} \right)$$

$$K_{sp} = 4.92874705 \times 10^{-13} \text{ mol}^2 \text{ kg}^{-2}$$

$$\boxed{K_{sp} = 4.929 \times 10^{-13} \text{ mol}^2 \text{ kg}^{-2}}$$

The solubility is therefore,

$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = s^2$$

$$s = \sqrt{K_{\text{sp}}}$$

$$s = \sqrt{4.928\,747\,05 \times 10^{-13} \text{ mol}^2 \text{ kg}^{-2}}$$

$$s = 7.020\,503\,58 \times 10^{-7} \text{ mol kg}^{-1}$$

$$\boxed{s = 7.021 \times 10^{-7} \text{ mol kg}^{-1}}$$

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**8.39.** The emf of a cell



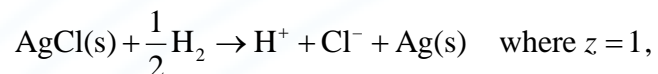
was found to be 0.517 V at 25 °C. Calculate the pH of the HCl solution.

**Solution:**

Given:  $E = 0.517 \text{ V}$ ,  $T = 25 \text{ °C}$

Required: pH

From Table 8.1, the standard emf of the AgCl|Ag electrode is 0.222 33 V and the cell reaction is:



To calculate the pH, we first need to find the concentration of  $\text{H}^+$  ions.

Using Eq. 8.13,

$$E = E^\circ - \frac{RT}{F} \ln([\text{H}^+][\text{Cl}^-])^u$$

$$\ln([\text{H}^+][\text{Cl}^-])^u = \frac{E - E^\circ}{-0.0257}$$

$$([\text{H}^+][\text{Cl}^-])^u = \exp\left(\frac{E - E^\circ}{-0.0257}\right)$$

$$([\text{H}^+][\text{Cl}^-])^u = \exp\left(\frac{0.22233 \text{ V} - 0.517 \text{ V}}{-0.0257}\right)$$

$$([\text{H}^+][\text{Cl}^-])^u = 95\,392.83\,548 \text{ mol}^2 \text{ dm}^{-6}$$

Since the concentrations of  $\text{H}^+$  and  $\text{Cl}^-$  are the same,



$$[\text{H}^+] = [\text{Cl}^-]$$

$$[\text{H}^+] = \sqrt{95\,392.835\,48 \text{ mol}^2 \text{ dm}^{-6}}$$

$$[\text{H}^+] = 308.857\,306 \text{ mol dm}^{-3}$$

The pH is given by the logarithm of the hydrogen ion concentration

$$\text{pH} = \log [\text{H}^+]$$

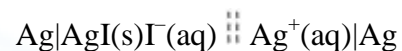
$$\text{pH} = \log (308.857\,306 \text{ mol dm}^{-3})$$

$$\text{pH} = 2.489\,757\,879$$

$$\boxed{\text{pH} = 2.48}$$

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**8.40.** The emf of the cell

is  $-0.9509\text{ V}$  at  $25\text{ }^{\circ}\text{C}$ . Calculate the solubility and the solubility product of AgI at that temperature.

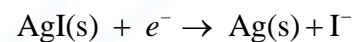
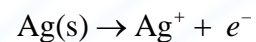
**Solution:**

Given:  $E = -0.9509\text{ V}$ ,  $T = 25\text{ }^{\circ}\text{C}$

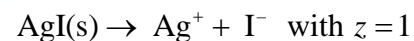
Required:  $s$ ,  $K_{\text{sp}}$

To solve this problem, we follow the example set in problem 8.38

The half reactions for each electrode are:



The reaction of interest is given by,



We can calculate the solubility product from Eq. 8.13,

$$E^{\circ} = 0.0257 \ln ([\text{Ag}^+][\text{I}^-])^u$$

$$K_{sp} = [\text{Ag}^+][\text{I}^-]$$

$$E^{\circ} = 0.0257 \ln K_{sp}$$

$$K_{sp} = \exp\left(\frac{E^{\circ}}{0.0257}\right)$$

$$K_{sp} = \exp\left(\frac{-0.9509}{0.0257}\right)$$

$$K_{sp} = 8.53\,304\,763 \times 10^{-17} \text{ mol}^2 \text{ kg}^{-2}$$

$$\boxed{K_{sp} = 8.533 \times 10^{-17} \text{ mol}^2 \text{ kg}^{-2}}$$

The solubility is therefore,

$$K_{sp} = [\text{Ag}^+][\text{I}^-] = s^2$$

$$s = \sqrt{K_{sp}}$$

$$s = \sqrt{8.533\,047\,63 \times 10^{-17} \text{ mol}^2 \text{ kg}^{-2}}$$

$$s = 9.237\,449\,662 \times 10^{-9} \text{ mol kg}^{-1}$$

$$\boxed{s = 9.237 \times 10^{-9} \text{ mol kg}^{-1}}$$

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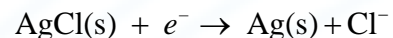
**8.41.** An electrochemical cell  $M(s)|MCl(aq, 1.0\ m)|AgCl(s)|Ag(s)$ , where  $MCl$  is the chloride salt of the metal electrode  $M$ , yields a cell potential of 0.2053 V at 25 °C. What is the mean activity coefficient  $\gamma_{\pm}$  of the electrolyte  $MCl$ ?  $E^{\circ}$  for the  $M(s)|M^{+}$  electrode is 0.0254 V.

**Solution:**

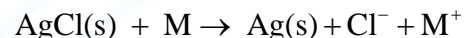
Given:  $E = 0.2053\ V$ ,  $T = 25\ ^{\circ}C$ ,  $E^{\circ} = 0.0254\ V$

Required:  $\gamma_{\pm}$

The half reactions for each electrode are:



And the overall reaction is given by,



$$E^{\circ} = 0.222\ 33\ V - 0.0254\ V$$

$$E^{\circ} = 0.196\ 93\ V$$

To solve for the activity coefficient, we use Eq. 8.43

$$E + \frac{2RT}{F} \ln m^{\prime\prime} = E^{\circ} - \frac{2RT}{F} \ln \gamma_{\pm}$$

Since the molality of  $MCl$  is exactly 1, this expression simplifies to,

$$E + \cancel{\frac{2RT}{F} \ln 1} = E^{\circ} - \frac{2RT}{F} \ln \gamma_{\pm}$$

$$E = E^{\circ} - \frac{2RT}{F} \ln \gamma_{\pm}$$

Rearranging and solving for the mean activity coefficient, we obtain,

$$E = E^\circ - 2 \times 0.0257 \ln \gamma_{\pm}$$

$$\gamma_{\pm} = e^{\frac{E - E^\circ}{-2 \times 0.0257}}$$

$$\gamma_{\pm} = e^{\frac{0.2053 - 0.19693}{-2 \times 0.0257}}$$

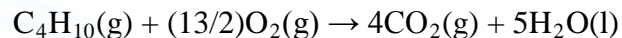
$$\gamma_{\pm} = 0.849\,726\,737\,1$$

$$\boxed{\gamma_{\pm} = 0.850}$$

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**8.42.** The following thermodynamic data apply to the complete oxidation of butane at 25 °C.



$$\Delta H^\circ = -2877 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -432.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

Suppose that a completely efficient fuel cell could be set up utilizing this reaction. Calculate (a) the maximum electrical work and (b) the maximum total work that could be obtained at 25 °C.

**Solution:**

Given:  $\Delta H^\circ = -2877 \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = -432.7 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 25^\circ\text{C}$

Required: see above

a. The maximum electrical work for the fuel cell is  $-\Delta G^\circ$ .

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -2877 \times 10^3 \text{ J mol}^{-1} - (298.15 \text{ K})(-432.7 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G^\circ = -2\,747\,990.495 \text{ J mol}^{-1}$$

$$\Delta G^\circ = -2748 \text{ kJ mol}^{-1}$$

$$\text{electrical work} = -\Delta G^\circ$$

$$\boxed{\text{electrical work} = 2748 \text{ kJ mol}^{-1}}$$

b. The maximum total work that can be obtained is  $-\Delta A$

$$\Delta G^\circ = \Delta A^\circ - \sum \nu RT$$

$$\Delta A^\circ = \Delta G^\circ + \sum \nu RT$$

$$\sum \nu = 4 - 1 - \frac{13}{2}$$

$$\sum \nu = -3.5$$

$$\Delta A^\circ = -2747\,990.495 \text{ J mol}^{-1} + (-3.5)(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})$$

$$\Delta A^\circ = -2756\,666.884 \text{ J mol}^{-1}$$

$$\Delta A^\circ = -2758 \text{ kJ mol}^{-1}$$

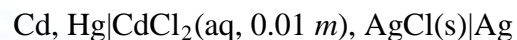
$$\text{total work} = \Delta A^\circ$$

$$\boxed{\text{total work} = 2758 \text{ kJ mol}^{-1}}$$

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**\*8.43.** At 298 K the emf of the cell



is 0.7585 V. The standard emf of the cell is 0.5732 V.

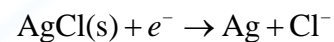
- Calculate the mean activity coefficient for the  $\text{Cd}^{2+}$  and  $\text{Cl}^-$  ions.
- Compare the value with that estimated from the Debye-Hückel limiting law, and comment on any difference.

**Solution:**

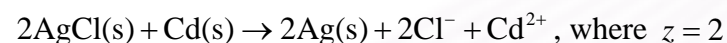
Given:  $E = 0.7585\text{ V}$ ,  $E^\circ = 0.5732\text{ V}$

Required: see above

- To calculate the mean activity coefficients, we follow a similar process as used in problem 8.24. The half reactions at each electrode are,



The overall reaction is given by,



Suppose that at 0.01  $m$  the activity coefficients are  $\gamma_+$  and  $\gamma_-$ , then we can solve for the mean activity coefficient from Eq. 8.40.



$$E = E^\circ - \frac{RT}{2F} \ln(a_{\text{Cd}^{2+}} a_{\text{Cl}^-}^2)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln(\gamma_+ [\text{Cd}^{2+}] \gamma_-^2 [\text{Cl}^-]^2)^u$$

$$E = E^\circ - \frac{RT}{2F} \ln([\text{Cd}^{2+}] [\text{Cl}^-]^2 \gamma_\pm^3)^u$$

$$0.7585 \text{ V} = 0.5732 \text{ V} - \frac{0.0257}{2} \ln((0.01)(0.02)^2 \gamma_\pm^3)$$

$$0.1853 = -0.01285 \ln(4 \times 10^{-6} \gamma_\pm^3)$$

$$\ln(4 \times 10^{-6} \gamma_\pm^3) = -14.42023346$$

$$(4 \times 10^{-6}) \gamma_\pm^3 = 5.462257621 \times 10^{-7}$$

$$\gamma_\pm = 0.5149567193$$

$$\boxed{\gamma_\pm = 0.51}$$

b. To calculate the activity coefficient according to the DHLL, we first calculate the ionic strength of the solution from Eq. 7.103,

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

$$I = \frac{1}{2} (1^2 \times 0.02 + 2^2 \times 0.01)$$

$$I = 0.03 \text{ m}$$

Now we rearrange the Debye-Hückel limiting law given by Eq. 7.111,

$$\log_{10} \gamma_\pm = -0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}$$

$$\gamma_\pm = 10^{-0.51 z_+ |z_-| \sqrt{I / \text{mol dm}^{-3}}}$$

$$\gamma_\pm = 10^{-0.51(2 \times 1) \sqrt{0.03}}$$

$$\gamma_\pm = 0.6657801116$$

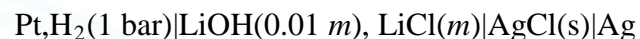
$$\boxed{\gamma_\pm = 0.67}$$

There is a considerable difference between the two methods.

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**\*8.44.** The following emf values were obtained by H. S. Harned and Copson [*J. Amer. Chem. Soc.*, 55, 2206(1933)] at 25 °C for the cell



at various molalities  $m$  of LiCl:

$m/\text{mol kg}^{-1}$	0.01	0.02	0.05	0.10	0.20
$E/\text{V}$	1.0498	1.0318	1.0076	1.9888	0.9696

Obtain from these data the ionic product of water.

**Solution:**

Given: emf values above

Required:  $K_w$

In this cell, we see that the LiOH is required for the hydrogen electrode, and the LiCl salt is used to complete the AgCl electrode. Both the  $\text{Cl}^-$  ion and the  $\text{H}^+$  ion will behave according to their activities in solution. We begin solving the problem by first determining the emf of the cell:

$$E_{\text{cell}} = E_{\text{AgCl}} - E_{\text{H}_2}$$

$$E_{\text{cell}} = E_{\text{AgCl}}^\circ - \frac{RT}{F} \ln a_{\text{Cl}^-} - \frac{RT}{F} \ln a_{\text{H}^+}$$

Since  $K_w = a_{\text{H}^+} a_{\text{OH}^-}$ , we can substitute this into the above expression and develop a relationship involving  $K_w$ .

$$E_{\text{cell}} = E_{\text{AgCl}}^\circ - \frac{RT}{F} \ln a_{\text{Cl}^-} - \frac{RT}{F} \ln \frac{K_w}{a_{\text{OH}^-}}$$

$$E_{\text{cell}} = E_{\text{AgCl}}^\circ - \frac{RT}{F} \ln a_{\text{Cl}^-} - \frac{RT}{F} \ln K_w + \frac{RT}{F} \ln a_{\text{OH}^-}$$

$$E_{\text{cell}} = E_{\text{AgCl}}^\circ - \frac{RT}{F} \ln \frac{a_{\text{Cl}^-}}{a_{\text{OH}^-}} - \frac{RT}{F} \ln K_w$$

Rewriting this expression in terms of activity coefficients and molalities gives,

$$E_{\text{cell}} = E_{\text{AgCl}}^{\circ} - \frac{RT}{F} \ln \frac{m_{\text{Cl}^-} \gamma_{\text{Cl}^-}}{m_{\text{OH}^-} \gamma_{\text{OH}^-}} - \frac{RT}{F} \ln K_w$$

$$E_{\text{cell}} - E_{\text{AgCl}}^{\circ} = -\frac{RT}{F} \ln \frac{m_{\text{Cl}^-}}{m_{\text{OH}^-}} - \frac{RT}{F} \ln \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{OH}^-}} - \frac{RT}{F} \ln K_w$$

$$\frac{E_{\text{cell}} - E_{\text{AgCl}}^{\circ}}{0.0257} = -\ln \frac{m_{\text{Cl}^-}}{m_{\text{OH}^-}} - \ln \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{OH}^-}} - \ln K_w$$

The molality of  $\text{OH}^-$  is given as  $0.01\text{ m}$ , and from Table 8.1,  $E_{\text{AgCl}}^{\circ} = 0.222\,33\text{ V}$ .

$$\frac{E_{\text{cell}} - 0.222\,33}{0.0257} + \ln \frac{m_{\text{Cl}^-}}{0.01} = -\ln \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{OH}^-}} - \ln K_w$$

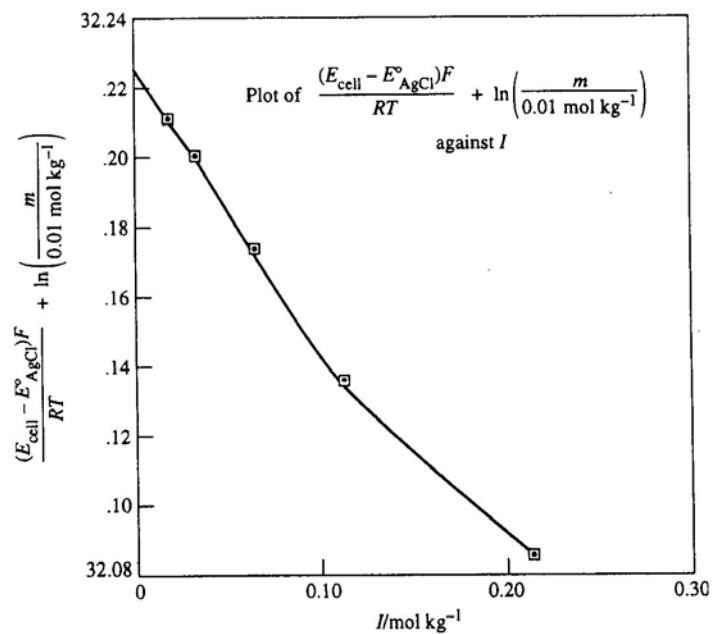
We plot the left-hand side of the equation against the ionic strength, which varies with concentration, and extrapolate to zero ionic strength. At zero ionic strength, the activity coefficients approach unity. Then the value of the curve is  $-\ln K_w$ .

$$\frac{E_{\text{cell}} - 0.222\,33}{0.0257} + \ln \frac{m_{\text{Cl}^-}}{0.01} = -\ln K_w$$

In the following data,  $I$  is based on  $m + 0.01\text{ m OH}^-$ , where  $0.01\text{ m}$  is constant.

$m / \text{mol kg}^{-1}$	0.01	0.02	0.05	0.10	0.20
$I / \text{mol kg}^{-1}$	0.02	0.03	0.06	0.11	0.21
$\frac{E_{\text{cell}} - 0.222\,33}{0.0257}$	32.3086	31.5079	30.566	29.834	29.087
$\ln \frac{m}{0.01}$	0.000	0.693	1.609	2.303	2.996
$\frac{E_{\text{cell}} - 0.222\,33}{0.0257} + \ln \frac{m}{0.01}$	32.209	32.301	32.175	32.137	32.083

From the indicated plot shown, the value of  $-\ln K_w$  is  $1.010 \times 10^{-14}$ .



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CHAPTER 9

Chemical Kinetics I.  
The Basic Ideas

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Physical Chemistry

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Problems and Solutions

**Chapter 9**

*\*problems with an asterisk are slightly more demanding*

**Rate Constants and Order of Reaction**

**9.1.** The stoichiometric equation for the oxidation of bromide ions by hydrogen peroxide in acid solution is:



Since the reaction does not occur in one stage, the rate equation does not correspond to this stoichiometric equation but is

$$v = k[\text{H}_2\text{O}_2][\text{H}^+][\text{Br}^-]$$

- If the concentration of  $\text{H}_2\text{O}_2$  is increased by a factor of 3, by what factor is the rate of consumption of  $\text{Br}^-$  ions increased?
- If the rate of consumption of  $\text{Br}^-$  ions is  $7.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ , what is the rate of consumption of hydrogen peroxide? What is the rate of formation of bromine?
- What is the effect on the rate constant  $k$  of increasing the concentration of bromide ions?
- If by the addition of water to the reaction mixture the total volume were doubled, what would be the effect on the rate of change of the concentration of  $\text{Br}^-$ ? What would be the effect on the rate constant  $k$ ?

[Solution](#)

**9.2.** A reaction obeys the stoichiometric equation:



Rates of formation of Z at various concentrations of A and B are as follows:

[A]/mol dm <sup>-3</sup>	[B]/mol dm <sup>-3</sup>	Rate/mol dm <sup>-3</sup> s <sup>-1</sup>
$3.5 \times 10^{-2}$	$2.3 \times 10^{-2}$	$5.0 \times 10^{-7}$
$7.0 \times 10^{-2}$	$4.6 \times 10^{-2}$	$2.0 \times 10^{-6}$
$7.0 \times 10^{-2}$	$9.2 \times 10^{-2}$	$4.0 \times 10^{-6}$

What are  $\alpha$  and  $\beta$  in the rate equation and what is the rate constant  $k$ ?

$$v = k[A]^\alpha[B]^\beta$$

[Solution](#)

- 9.3.** Some results for the rate of a reaction between two substances A and B are shown in the following table. Deduce the order  $\alpha$  with respect to A, the order  $\beta$  with respect to B, and the rate constant.

[A]/mol dm <sup>-3</sup>	[B]/mol dm <sup>-3</sup>	Rate/mol dm <sup>-3</sup> s <sup>-1</sup>
$1.4 \times 10^{-2}$	$2.3 \times 10^{-2}$	$7.40 \times 10^{-9}$
$2.8 \times 10^{-2}$	$4.6 \times 10^{-2}$	$5.92 \times 10^{-8}$
$2.8 \times 10^{-1}$	$4.6 \times 10^{-2}$	$5.92 \times 10^{-6}$

[Solution](#)

- 9.4.** A substance decomposes at 600 K with a rate constant of  $3.72 \times 10^{-5} \text{ s}^{-1}$ .

- Calculate the half-life of the reaction.
- What fraction will remain undecomposed if the substance is heated for 3 h at 600 K?

[Solution](#)

- 9.5.** How does the time required for a first-order reaction to go to 99% completion relate to the half-life of the reaction?

[Solution](#)

- 9.6.** The rate constant for the reaction  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$  is  $1.3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate the half-life for the neutralization process if (a)  $[\text{H}^+] = [\text{OH}^-] = 10^{-1} \text{ M}$  and (b)  $[\text{H}^+] = [\text{OH}^-] = 10^{-4} \text{ M}$ .

[Solution](#)

- 9.7.** The isotope  $^{90}\text{Sr}$  emits radiation by a first-order process (as is always the case with radioactive decay) and has a half-life of 28.1 years. When ingested by mammals it becomes permanently incorporated in bone tissue. If 1  $\mu\text{g}$  is absorbed at birth, how much of this isotope remains after (a) 25 years, (b) 50 years, (c) 70 years?

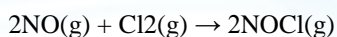
[Solution](#)



- 9.8.** The first-order decomposition of nitramide in the presence of bases,  $\text{NH}_2\text{NO}_2 \rightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$ , is conveniently analyzed by collecting the gas evolved during the reaction. During an experiment, 50.0 mg of nitramide was allowed to decompose at 15 °C. The volume of dry gas evolved after 70.0 min. was measured to be 6.59 cm<sup>3</sup> at 1 bar pressure. Find the rate constant and the half-life for nitramide decomposition.

[Solution](#)

- 9.9.** The reaction:



is second order in NO and first order in Cl<sub>2</sub>. In a volume of 2 dm<sup>3</sup>, 5 mol of nitric oxide and 2 mol of Cl<sub>2</sub> were brought together, and the initial rate was  $2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ . What will be the rate when one-half of the chlorine has reacted?

[Solution](#)

- 9.10.** Measuring the total pressure is a convenient way to monitor the gas phase reaction:



However, the rate depends on the concentration of the reactant, which is proportional to the partial pressure of the reactant. Derive an expression relating the rate of this reaction to the initial pressure,  $P_0$ , and the total pressure,  $P_t$ , at time  $t$ . Assume that the reaction follows second-order kinetics.

[Solution](#)

- 9.11.** The following results were obtained for the rate of decomposition of acetaldehyde:

% decomposed:

0	5	10	15	20	25	30	35	40	45	50
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Rate/Torr min<sup>-1</sup>

8.53	7.49	6.74	5.90	5.14	4.69	4.31	3.75	3.11	2.67	2.29
------	------	------	------	------	------	------	------	------	------	------

Employ van't Hoff's differential method to obtain the order of reaction.

[Solution](#)

- 9.12.** The isotope  $^{32}_{15}\text{P}$  emits radiation and has a half-life of 14.3 days. Calculate the decay constant in  $\text{s}^{-1}$ . What percentage of the initial activity remains after (a) 10 days, (b) 20 days, (c) 100 days?

[Solution](#)

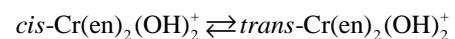
- 9.13.** The following counts per minute were recorded on a counter for the isotope  $^{35}_{16}\text{S}$  at various times:

Time/d	Counts/min
0	4280
1	4245
2	4212
3	4179
4	4146
5	4113
10	3952
15	3798

Determine the half-life in days and the decay constant in  $\text{s}^{-1}$ . How many counts per minute would be expected after (a) 60 days and (b) 365 days?

[Solution](#)

- 9.14.** The reaction:



is first order in both directions. At 25 °C the equilibrium constant is 0.16 and the rate constant  $k_1$  is  $3.3 \times 10^{-4} \text{ s}^{-1}$ . In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed?

[Solution](#)

- 9.15.** Suppose that a gas phase reaction  $2A(g) \rightarrow 2B(g) + C(g)$  follows second-order kinetics and goes to completion. If the reaction is allowed to proceed in a constant volume vessel at an initial pressure of 2 bar (only A is initially present), what will be the partial pressures of A, B, and C and the total pressure at  $t = t_{1/2}$ ,  $2t_{1/2}$ ,  $3t_{1/2}$ , and infinity?

[Solution](#)

- 9.16.** Derive the following relationship for the half-life  $t_{1/2}$  of a reaction of order  $n$ , with all reactants having an initial concentration  $a_0$ :

$$t_{1/2} = \frac{2^{n-1} - 1}{ka_0^{n-1}(n-1)}$$

[Solution](#)

- 9.17.** Vaughan [*J. Am. Chem. Soc.* 54, 3867(1932)] reported the following pressure measurements as a function of time for the dimerization of 1,3-butadiene ( $C_4H_6$ ) under constant volume conditions at 326 °C:

$t/\text{min}$	3.25	12.18	24.55	42.50	68.05
$P/\text{Torr}$	618.5	584.2	546.8	509.3	474.6

The initial amount of butadiene taken would have exerted a pressure of 632.0 Torr. Find whether the reaction follows first- or second-order kinetics and evaluate the rate constant.

[Solution](#)

- 9.18.** A drug administered to a patient is usually consumed by a first-order process. Suppose that a drug is administered in equal amounts at regular intervals and that the interval between successive doses is equal to the  $(1/n)$ -life for the disappearance process (i.e., to the time that it takes for the fraction  $1/n$  to disappear). Prove that the limiting concentration of the drug in the patient's body is equal to  $n$  times the concentration produced by an individual dose.

[Solution](#)

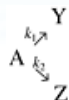
- 9.19.** Equation 9.45 applies to a second-order reaction of stoichiometry  $A + B \rightarrow Z$ . Derive the corresponding equation for a second-order reaction of stoichiometry  $2A + B \rightarrow Z$ .

[Solution](#)

- 9.20.** Derive the integrated rate equation for an irreversible reaction of stoichiometry  $2A + B \rightarrow Z$ , the rate being proportional to  $[A]^2[B]$  and the reactants present in stoichiometric proportions; take the initial concentration of A as  $2a_0$  and that of B as  $a_0$ . Obtain an expression for the half-life of the reaction.

[Solution](#)

- 9.21.** Prove that for two simultaneous (parallel) reactions



$$\frac{[Y]}{[Z]} = \frac{k_1}{k_2} \text{ at all times.}$$

[Solution](#)

- \*9.22.** Prove that for two consecutive first-order reactions;  $A \rightarrow B \rightarrow C$  the rate of formation of C is given by:

$$[C] = [A]_0 \left( 1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} \right)$$

where  $[A]_0$  is the initial concentration of A.

(Hint: The solution of the differential equation):

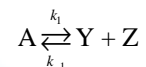
$$\frac{dx}{dt} = abe^{-bt} - cx$$

where  $a$ ,  $b$ , and  $c$  are constants, is

$$x = \frac{ab}{c-b} (e^{-bt} - e^{-ct}) + I$$

[Solution](#)

**\*9.23. a.** Derive the integrated rate equation for a reversible reaction of stoichiometry:



The reaction is first order from left to right and second order from right to left. Take the initial concentration of A as  $a_0$  and the concentration at time  $t$  as  $a_0 - x$ .

**b.** Obtain the integrated equation in terms of  $k$ , and the equilibrium constant  $K = k_1/k_{-1}$ .

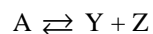
**c.** A reaction to which this rate equation applies is the hydrolysis of methyl acetate. Newling and Hinshelwood, *J. Chem. Soc.*, 1936, 1357(1936), obtained the following results for the hydrolysis of 0.05  $M$  ester at 80.2 °C in the presence of 0.05  $M$  HCl, which catalyzes the reaction:

Time, s	1350	2070	3060	5340	7740	$\infty$
Percent hydrolysis	21.2	30.7	43.4	59.5	73.45	90.0

Obtain values for the rate constants  $k_1$  and  $k_{-1}$ .

[Solution](#)

**\*9.24.** The dissociation of a weak acid  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$  can be represented as:



The rate constants  $k_1$  and  $k_{-1}$  cannot be measured by conventional methods but can be measured by the T-jump technique (Section 9.5). Prove that the relaxation time is given by:

$$t^* = \frac{1}{k_1 + 2k_{-1}x_e}$$

where the concentration of the ions (Y and Z) is at equilibrium.

[Solution](#)

**Temperature Dependence**

**9.25.** The rate constant for a reaction at 30 °C is found to be exactly twice the value at 20 °C. Calculate the activation energy.

[Solution](#)

**9.26.** The rate constant for a reaction at 230 °C is found to be exactly twice the value at 220 °C. Calculate the activation energy.

[Solution](#)

**9.27.** The following data for a first-order decomposition reaction in aqueous medium was reported by E. O. Wiig [*J. Phys. Chem.* 34, 596(1930)].

$t/^{\circ}\text{C}$	0	20	40	60
$k/10^{-5} \text{ min}^{-1}$	2.46	43.5	575	5480

Find the activation energy and the preexponential factor.

[Solution](#)

**9.28.** Two second-order reactions have identical preexponential factors and activation energies differing by 20.0 kJ mol<sup>-1</sup>. Calculate the ratio of their rate constants (a) at 0 °C and (b) at 1000 °C.

[Solution](#)

**9.29.** The gas-phase reaction between nitric oxide and oxygen is third order. The following rate constants have been measured:

$T/\text{K}$	80.0	143.0	228.0	300.0	413.0	564.0
$k \times 10^9/\text{cm}^6 \text{ mol}^{-1} \text{ s}^{-1}$	41.8	20.2	10.1	7.1	4.0	2.8

The behavior is interpreted in terms of a temperature-dependent preexponential factor; the rate equation is of the form:

$$k = aT^n e^{-E/RT}$$

where  $a$  and  $n$  are constants. Assume the activation energy to be zero and determine  $n$  to the nearest half-integer.

[Solution](#)

**9.30.** The definition of activation energy  $E_a$  is generally considered to be given by an extension of Eq. 9.91:

$$E_a = RT^2 \left( \frac{d \ln k}{dT} \right)$$

Problem 9.29 shows that for certain reactions, the temperature dependence of the reaction rate constant is better described by an expression of the type

$$k = aT^n e^{-E/RT}$$

Using the definition for  $E_a$  given here, derive an expression for the activation energy from this expression.

[Solution](#)

**9.31.** The water flea *Daphnia* performs a constant number of heartbeats and then dies. The flea lives twice as long at 15 °C as at 25 °C. Calculate the activation energy for the reaction that controls the rate of its heartbeat.

[Solution](#)

**9.32.** A sample of milk kept at 25 °C is found to sour 40 times as rapidly as when it is kept at 4 °C. Estimate the activation energy for the souring process.

[Solution](#)

**\*9.33.** Experimentally, the rate constant for the  $\text{O}(^3\text{P}) + \text{HCl}$  reaction in the gas phase is found to have a temperature dependence given by:

$$k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 5.6 \times 10^{-21} T^{2.87} e^{-1766 \text{ K}/T}$$

in the range 350 – 1480 K [Mahmud, Kim, and Fontijn, *J. Phys. Chem.* 94, 2994(1990)].

**a.** Using the results of Problem 9.30, find the value of  $E_a$  at 900 K, which is approximately the middle of this range.

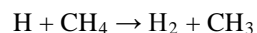
**b.** Using variational transition-state theory (an extension of the transition-state theory described in Section 9.9), the theoretical rate constant for this reaction is found to behave according to the equation:

$$k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 6.9 \times 10^{-20} T^{2.60} e^{-2454 \text{ K}/T}$$

in the same temperature range [T. C. Allison, B. Ramachandran, J. Senekowitsch, D. G. Truhlar, and R. E. Wyatt, *J. Mol. Structure, Theochem*, **454**, 307, 1998.] Compare the experimental and theoretical rate constants at 900 K.

[Solution](#)

**9.34.** The activation energy for the reaction:



has been measured to be  $49.8 \text{ kJ mol}^{-1}$ . Some estimates of enthalpies of formation,  $\Delta_f H^\circ$ , are:

H	$218.0 \text{ kJ mol}^{-1}$
CH <sub>4</sub>	$-74.8 \text{ kJ mol}^{-1}$
CH <sub>3</sub>	$139.5 \text{ kJ mol}^{-1}$

Estimate a value for the activation energy of the reverse reaction.

[Solution](#)

**\*9.35.** By a treatment similar to that given for relaxation methods for the case  $\text{A} \rightleftharpoons \text{Z}$ , derive the rate equations for analyzing the reaction  $\text{A} + \text{B} \rightleftharpoons \text{Z}$  by carrying out the steps below.

**a.** Show that at equilibrium,  $k_1 a_e b_e = k_{-1} z_e$ , where the subscript  $e$  indicates equilibrium concentrations.

**b.** Show that  $\frac{dx}{dt} = k_1(a_e - x)(b_e - x) - k_{-1}(z_e + x)$ , where  $x$  represents a change from equilibrium.

**c.** Show that for small  $x$ ,  $\frac{dx}{dt} = -[k_1(a_e + b_e) + k_{-1}]x$ . [*Hint:* Use the result of part (a).]

**d.** The displacement from equilibrium  $x$  always follows the first-order process  $x = x_0 \exp(-t/t^*)$ , where  $t^*$  is the relaxation time. Show that  $dx/dt = -x/t^*$ .

**e.** Comparing the results of parts (c) and (d), show that  $\frac{1}{t^*} = 2k_1 a_e + k_{-1}$  if  $a_e = b_e$ .

**f.** For the case  $a_e = b_e$ , show that  $\frac{1}{t^*} = 2\sqrt{k_1 k_{-1} z_e} + k_{-1}$ . [*Hint:* Use the result of part (e) and the fact that  $\frac{k_1}{k_{-1}} = \frac{z_e}{a_e b_e}$ .]

[Solution](#)



**9.36.** A reaction of the type  $A + B \rightleftharpoons Z$  has been studied by relaxation methods. Some of the available data relating equilibrium concentrations of the product to the relaxation times are given below.

$z_e/M$	0.001	0.002	0.005	0.010	0.025	0.05	0.10
$t^*/ms$	4.08	3.74	2.63	1.84	1.31	0.88	0.674

Determine  $k_1$ ,  $k_{-1}$ , and  $K = k_1/k_{-1}$ .

[Solution](#)

**9.37.** The equilibrium  $H_2O \rightleftharpoons H^+ + OH^-$  has a relaxation time of about  $40 \mu s$  at  $25^\circ C$ . Find the values of the forward and reverse rate constants.  $K_w = [H^+][OH^-] = 10^{-14}$ .

(Hint: For this case, using steps similar to those of Problem 9.25, it can be shown that  $\frac{1}{t^*} = k_1 + k_{-1}([H^+]_e + [OH^-]_e)$ .)

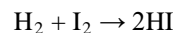
[Solution](#)

### Collision Theory and Transition-State Theory

**9.38.** Two reactions of the same order have identical activation energies and their entropies of activation differ by  $50 J K^{-1} mol^{-1}$ . Calculate the ratio of their rate constants at any temperature.

[Solution](#)

**9.39.** The gas-phase reaction:



is second order. Its rate constant at  $400^\circ C$  is  $2.34 \times 10^{-2} dm^3 mol^{-1} s^{-1}$ , and its activation energy is  $150 kJ mol^{-1}$ . Calculate  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$ , and  $\Delta^\ddagger G^\circ$  at  $400^\circ C$ , and the preexponential factor.

[Solution](#)

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**9.40.** A substance decomposes according to first-order kinetics; the rate constants at various temperatures are as follows:

Temperature/°C	Rate constant, $k/s^{-1}$
15.0	$4.18 \times 10^{-6}$
20.0	$7.62 \times 10^{-6}$
25.0	$1.37 \times 10^{-5}$
30.0	$2.41 \times 10^{-5}$
37.0	$5.15 \times 10^{-5}$

Calculate the activation energy. Calculate also, at 25 °C, the enthalpy of activation, the Gibbs energy of activation, the preexponential factor, and the entropy of activation.

[Solution](#)

**9.41.** The following data have been obtained for the hydrolysis of adenosine triphosphate, catalyzed by hydrogen ions:

Temperature/°C	Rate constant, $k/s^{-1}$
39.9	$4.67 \times 10^{-6}$
43.8	$7.22 \times 10^{-6}$
47.1	$10.0 \times 10^{-6}$
50.2	$13.9 \times 10^{-6}$

Calculate, at 40 °C, the Gibbs energy of activation, the energy of activation, the enthalpy of activation, the preexponential factor, and the entropy of activation.

[Solution](#)

**9.42.** The half-life of the thermal denaturation of hemoglobin, a first-order process, has been found to be 3460 s at 60 °C and 530 s at 65 °C. Calculate the enthalpy of activation and entropy of activation at 60 °C, assuming the Arrhenius equation to apply.

[Solution](#)

**\*9.43. a.** Using Eq. 9.73, calculate the collision density for  $6.022 \times 10^{23}$  molecules of hydrogen iodide present in a volume  $1 \text{ m}^3$  at 300 K. Take  $d_{\text{AA}} = 0.35 \text{ nm}$ .

**b.** If the activation energy for the decomposition of HI is  $184 \text{ kJ mol}^{-1}$ , what rate constant does kinetic theory predict at  $300^\circ\text{C}$ ? To what entropy of activation does this result correspond?

[Solution](#)

**9.44.** The rate constant for a first-order reaction is  $7.40 \times 10^{-9} \text{ s}^{-1}$  at  $25^\circ\text{C}$ , and the activation energy is  $112.0 \text{ kJ mol}^{-1}$ . Calculate, at  $25^\circ\text{C}$ , the preexponential factor  $A$ , the enthalpy of activation  $\Delta^\ddagger H^\circ$ , the Gibbs energy of activation  $\Delta^\ddagger G^\circ$ , and the entropy of activation  $\Delta^\ddagger S^\circ$ .

[Solution](#)

**9.45.** The rate constant for a second-order reaction in solution is  $3.95 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ , and the activation energy is  $120.0 \text{ kJ mol}^{-1}$ . Calculate, at  $25^\circ\text{C}$ , the preexponential factor  $A$ , the enthalpy of activation  $\Delta^\ddagger H^\circ$ , the Gibbs energy of activation  $\Delta^\ddagger G^\circ$ , and the entropy of activation  $\Delta^\ddagger S^\circ$ .

[Solution](#)

### Ionic-Strength Effects

**9.46.** The rate constant  $k$  for the reaction between persulfate ions and iodide ions varies with ionic strength  $I$  as follows:

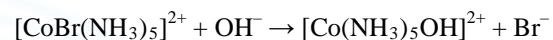
$I/10^{-3} \text{ mol dm}^{-3}$	2.45	3.65	4.45	6.45	8.45	12.4
$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.05	1.12	1.16	1.18	1.26	1.39

Estimate the value of  $z_{\text{A}}z_{\text{B}}$ .

[Solution](#)

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**9.47.** The following constants were obtained by Brønsted and Livingstone [*J. Amer. Chem. Soc.*, 49, 435(1927)] for the reaction:



under the following conditions:

$[\text{CoBr}(\text{NH}_3)_5]^{2+}$	Concentration/mol dm <sup>-1</sup>		$k$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
	NaOH	NaCl	
$5.0 \times 10^{-4}$	$7.95 \times 10^{-4}$	0	1.52
$5.96 \times 10^{-4}$	$1.004 \times 10^{-3}$	0	1.45
$6.00 \times 10^{-4}$	$0.696 \times 10^{-3}$	0.005	1.23
$6.00 \times 10^{-4}$	$0.696 \times 10^{-3}$	0.020	0.97
$6.00 \times 10^{-4}$	$0.691 \times 10^{-3}$	0.030	0.91

Make an estimate of the rate constant of the reaction at zero ionic strength. Are the results consistent with  $z_A z_B = -2$ ?

[Solution](#)

**9.48.** Suppose that the rates of ionic reactions in solution were proportional to the activity rather than the concentration of activated complexes. Derive an equation relating the logarithm of the rate constant to the ionic strength and the charge numbers of the ions and contrast it with Eq. 9.124. Can the results in Figure 9.22 be reconciled with the equation you have derived?

[Solution](#)

- 9.49.** When the subatomic species muonium (Mu) was first discovered in 1960, it was not known whether it bore an electric charge. The answer was provided by a kinetic study of the ionic strength effect on the reaction  $\text{Mu} + \text{Cu}^{2+}$  in aqueous solution. The following rate constants were measured at two ionic strengths:

$$\begin{array}{ll} I = 0 & k = 6.50 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ I = 0.9 \text{ M} & k = 6.35 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{array}$$

Suppose that muonium had a single negative charge; what would  $k$  be expected to be at an ionic strength of  $0.9 \text{ M}$ ? What do you deduce about the actual charge on muonium?

[Solution](#)

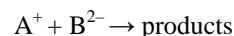
- 9.50.** The rate constants of a second-order reaction in aqueous solution at  $25^\circ\text{C}$  had the following values at two ionic strengths:

$I/\text{mol dm}^{-3}$	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$2.5 \times 10^{-3}$	$1.40 \times 10^{-3}$
$2.5 \times 10^{-2}$	$2.35 \times 10^{-3}$

Make an estimate of the value of  $z_A z_B$ , the product of the charge numbers.

[Solution](#)

- 9.51.** A reaction of the type:



was found at  $25^\circ\text{C}$  to have a rate constant of  $2.8 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at an ionic strength of  $1.0 \times 10^{-3} \text{ M}$ . Assume the Debye-Hückel limiting law to apply and estimate the rate constant at zero ionic strength.

[Solution](#)

### Pressure Effects

- 9.52.** The rate of a reaction at  $300 \text{ K}$  is doubled when the pressure is increased from  $1 \text{ bar}$  to  $2000 \text{ bar}$ . Calculate  $\Delta^\ddagger V^\circ$ , assuming it to be independent of pressure.

[Solution](#)

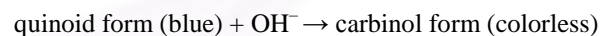
**9.53.** The following results were obtained for the solvolysis of benzyl chloride in an acetone-water solution at 25 °C:

$P/10^2 \text{ kPa}$	1.00	345	689	1033
$k/10^{-6} \text{ s}^{-1}$	7.18	9.58	12.2	15.8

Make an appropriate plot and estimate  $\Delta^\ddagger V^\circ$ .

[Solution](#)

**9.54.** The fading of bromphenol blue in alkaline solution is a second-order reaction between hydroxide ions and the quinoid form of the dye:



The following results show the variation of the second-order rate constant  $k$  with the hydrostatic pressure  $P$  at 25 °C:

$P/10^4 \text{ kPa}$	101.3	2.76	5.51	8.27	11.02
$k/10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	9.30	11.13	13.1	15.3	17.9

Estimate  $\Delta^\ddagger V^\circ$ .

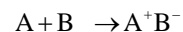
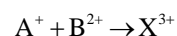
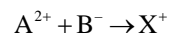
[Solution](#)

**9.55.** Use Figure 9.23 to make approximate estimates of the volumes of activation for the alkaline hydrolyses of methyl acetate, ethyl acetate, and propionamide, at 25 °C.

[Solution](#)

**Essay Questions**

- 9.56.** Explain clearly the difference between the order and the molecularity of a reaction.
- 9.57.** Give an account of experimental methods that might be used to study the kinetics of (a) a reaction having a half-life of about  $10^{-1}$  s and (b) a reaction having a half-life of about  $10^{-7}$  s.
- 9.58.** Predict the effects of (a) increasing the dielectric constant of the solvent, (b) increasing the ionic strength, and (c) increasing the pressure on the reactions of the following types:



Give a clear explanation in each case. What can you say about the entropy of activation to be expected in each case?

- 9.59.** Van't Hoff's differential method can be applied to kinetic data in two different ways:
1. Rates can be determined at various stages of a single reaction.
  2. Initial rates can be measured at a variety of initial concentrations, the reaction being run a number of times. In each case  $\log_{10}$  (rate) can be plotted against  $\log_{10}$  (concentration of a reactant). Can you suggest why a different order of reaction might be obtained when these two different procedures are used?

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**Solutions**

**9.1.** The stoichiometric equation for the oxidation of bromide ions by hydrogen peroxide in acid solution is:



Since the reaction does not occur in one stage, the rate equation does not correspond to this stoichiometric equation but is

$$v = k[\text{H}_2\text{O}_2][\text{H}^+][\text{Br}^-]$$

- If the concentration of  $\text{H}_2\text{O}_2$  is increased by a factor of 3, by what factor is the rate of consumption of  $\text{Br}^-$  ions increased?
- If the rate of consumption of  $\text{Br}^-$  ions is  $7.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ , what is the rate of consumption of hydrogen peroxide? What is the rate of formation of bromine?
- What is the effect on the rate constant  $k$  of increasing the concentration of bromide ions?
- If by the addition of water to the reaction mixture the total volume were doubled, what would be the effect on the rate of change of the concentration of  $\text{Br}^-$ ? What would be the effect on the rate constant  $k$ ?

**Solution:**

It is important to note that rather than considering the species as themselves, we can make the rate equation more simple by introducing the following substitutions.

$$\text{H}_2\text{O}_2 = \text{A}$$

$$\text{H}^+ = \text{B}$$

$$\text{Br}^- = \text{C}$$

- a)** We can start off by writing down the rate of reaction for each species involved. Recall from section 9.2 that the rate of reaction is independent of which reactant or product species is chosen. For the reaction:  $a\text{A} + b\text{B} \rightarrow y\text{Y} + z\text{Z}$  occurring at constant volume, the rate of reaction is given as;

$$v = -\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{y} \frac{d[\text{Y}]}{dt} = \frac{1}{z} \frac{d[\text{Z}]}{dt}$$

Let us now apply this to our particular case. This will yield;



$$v_A = -\frac{d[A]}{dt}, v_B = -\frac{1}{2} \frac{d[B]}{dt}, v_C = -\frac{1}{2} \frac{d[C]}{dt}$$

If the concentration of  $\text{H}_2\text{O}_2$  is increased by a factor of 3, then we can say that  $v_B$  will remain fixed and  $v_C$  will also increase by a factor of three.

$$v_C \text{ will } \uparrow \text{ by a factor of 3}$$

- b)** We are given that  $v_C = 7.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$  (bromide ion). With this information, we are able to determine the rate of consumption of species A and B. It is possible to also write the rate of reaction in a manner that expresses the rates of consumption or formation for each species.

$$v = \frac{v_A}{a} = \frac{v_B}{b} = \frac{v_Y}{y} = \frac{v_Z}{z}$$

$$v = \frac{v_A}{1} = \frac{v_C}{2} = \frac{v_{\text{Br}_2}}{1}$$

$$v = \frac{v_A}{1} = \frac{7.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}}{2} = \frac{v_{\text{Br}_2}}{1}$$

$$v_A = 0.0036 \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$v_A = 3.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$v_{\text{Br}_2} = 3.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

- c)** Recall from section 9.3 that the rate constant  $k$ , is independent of concentration (as well as time). This means that there will be no change in its value if one increases the concentration of bromide ions.

$$\text{no change in } k$$

- d)** If we add enough water into the mixture to double the total volume, we will at the same time, be diluting all of the concentrations by one half. Recall that for the bromide ion, we originally we have;

$$v_c = -\frac{1}{2} \frac{d[C]}{dt} \text{ multiplied by one half will produce } v_c = -\frac{1}{2} \frac{d[C]}{dt} \left( \frac{1}{2} \right) = -\frac{1}{4} \frac{d[C]}{dt}$$

$v_c$  will have a rate of disappearance that is 4x slower

no change in  $k$

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9.2. A reaction obeys the stoichiometric equation:



Rates of formation of Z at various concentrations of A and B are as follows:

[A]/mol dm <sup>-3</sup>	[B]/mol dm <sup>-3</sup>	Rate/mol dm <sup>-3</sup> s <sup>-1</sup>
$3.5 \times 10^{-2}$	$2.3 \times 10^{-2}$	$5.0 \times 10^{-7}$
$7.0 \times 10^{-2}$	$4.6 \times 10^{-2}$	$2.0 \times 10^{-6}$
$7.0 \times 10^{-2}$	$9.2 \times 10^{-2}$	$4.0 \times 10^{-6}$

What are  $\alpha$  and  $\beta$  in the rate equation and what is the rate constant  $k$ ?

$$v = k[A]^\alpha[B]^\beta$$

**Solution:**

Let us begin by determining the total order of the reaction by using the rate at a variety of concentrations.

$$v = \frac{v(C_3)}{v(C_2)} = \frac{4.0 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}}{2.0 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}}$$

$$v = 2$$

This tells us that the overall order of the reaction will be 2<sup>nd</sup> order. Since both A and B are included in the rate equation, we can assume that,

$$\boxed{\alpha = 1, \beta = 1}$$

$$v = k[A]^1[B]^1$$

The rate constant may be determined by rearranging the above expression and simply substituting in experimental values given above at the same concentration (for each species).

$$k = \frac{v}{[A]^1 [B]^1}$$

$$k = \frac{v(C_1)}{[A]^1 [B]^1} = \frac{5.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}}{(3.5 \times 10^{-2} \text{ mol dm}^{-3})(2.3 \times 10^{-2} \text{ mol dm}^{-3})}$$

$$k = 6.2 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

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**9.3.** Some results for the rate of a reaction between two substances A and B are shown in the following table. Deduce the order  $\alpha$  with respect to A, the order  $\beta$  with respect to B, and the rate constant.

	[A]/mol dm <sup>-3</sup>	[B]/mol dm <sup>-3</sup>	Rate/mol dm <sup>-3</sup> s <sup>-1</sup>
v <sub>1</sub>	1.4 × 10 <sup>-2</sup>	2.3 × 10 <sup>-2</sup>	7.40 × 10 <sup>-9</sup>
v <sub>2</sub>	2.8 × 10 <sup>-2</sup>	4.6 × 10 <sup>-2</sup>	5.92 × 10 <sup>-8</sup>
v <sub>3</sub>	2.8 × 10 <sup>-1</sup>	4.6 × 10 <sup>-2</sup>	5.92 × 10 <sup>-6</sup>

**Solution:**

Given: see above

Required:  $\alpha$ ,  $\beta$ ,  $k$

We will solve this problem in the same way that problem 9.2 was done.

Let us begin by determining the total order of the reaction by examining the concentrations of each species in conjunction with the change in the rate (at each different concentration).

1.

$$\frac{v_3}{v_2} = \left( \frac{2.8 \times 10^{-1}}{2.8 \times 10^{-2}} \right)^\alpha \left( \frac{4.6 \times 10^{-2}}{4.6 \times 10^{-2}} \right)^\beta$$

$$\left( \frac{5.92 \times 10^{-6}}{5.92 \times 10^{-8}} \right) = 10^\alpha = 100$$

$$\boxed{\alpha = 2}$$

2.

$$\frac{v_2}{v_1} = \left( \frac{2.8 \times 10^{-2}}{1.4 \times 10^{-2}} \right)^\alpha \left( \frac{4.6 \times 10^{-2}}{2.3 \times 10^{-2}} \right)^\beta$$

$$\left( \frac{5.92 \times 10^{-8}}{7.4 \times 10^{-9}} \right) = 8 = 4 \times 2^\beta$$

$$\boxed{\beta = 1}$$

3.

$$v = k[A]^2[B]$$

$$7.4 \times 10^{-9} = k_1 [1.4 \times 10^{-2}]^2 [2.3 \times 10^{-2}]$$

$$k_1 = 1.641\,526\,176 \times 10^{-3}$$

$$5.92 \times 10^{-8} = k_2 [2.8 \times 10^{-2}]^2 [4.6 \times 10^{-2}]$$

$$k_2 = 1.641\,526\,176 \times 10^{-3}$$

$$5.92 \times 10^{-6} = k_3 [2.8 \times 10^{-1}]^2 [4.6 \times 10^{-2}]$$

$$k_3 = 1.641\,526\,176 \times 10^{-3}$$

$$\bar{k} = \frac{k_1 + k_2 + k_3}{3}$$

$$\boxed{\bar{k} = 1.642 \times 10^{-3}}$$

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**9.4.** A substance decomposes at 600 K with a rate constant of  $3.72 \times 10^{-5} \text{ s}^{-1}$ .

**a.** Calculate the half-life of the reaction.

**b.** What fraction will remain undecomposed if the substance is heated for 3 h at 600 K?

**Solution:**

Given:  $T = 600 \text{ K}$ ,  $k = 3.72 \times 10^{-5} \text{ s}^{-1}$ ,  $t = 3 \text{ hrs}$

Required:  $t_{1/2}$ , fraction undecomposed

By looking at the units for the rate constant, it is often possible to determine the order of the reaction. This information will greatly facilitate the calculation of the half life as there are different equations that should be used depending on the order of the reaction. Since the units are in  $\text{s}^{-1}$ , we have seen in Table 9.1 that this corresponds to a 1<sup>st</sup> order reaction.

**a)** The half life will then be:

$$t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = \frac{\ln 2}{3.72 \times 10^{-5} \text{ s}^{-1}}$$

$$t_{1/2} = \frac{0.693147}{3.72 \times 10^{-5} \text{ s}^{-1}}$$

$$t_{1/2} = 18\,632.988\,72 \text{ s}$$

$$t_{1/2} = 1.86 \times 10^4 \text{ s}$$

$$t_{1/2} = 1.86 \times 10^4 \cancel{\text{ s}} \times \frac{1 \cancel{\text{ min}}}{60 \cancel{\text{ s}}} \times \frac{1 \text{ hr}}{60 \cancel{\text{ min}}}$$

$$t_{1/2} = 5.18 \text{ hrs}$$

**b)** The undecomposed fraction after three hours will be:

If  $k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}$  then we can rearrange this expression in order to solve for the fraction of substance that is undecomposed.

$$kt = \ln \frac{a_0}{a_0 - x}$$

$$\exp(kt) = \cancel{\ln} \left( \frac{a_0}{a_0 - x} \right)$$

$$\exp(-kt) = \frac{a_0 - x}{a_0} = \text{fraction undecomposed} = \exp \left( -3.72 \times 10^{-5} \cancel{s^{-1}} \times 3 \cancel{\text{hrs}} \times \frac{60 \cancel{\text{min}}}{1 \cancel{\text{hr}}} \times \frac{60 \cancel{s}}{1 \cancel{\text{min}}} \right) = 0.669$$

$$\boxed{\text{fraction undecomposed} = 0.669}$$

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**9.5.** How does the time required for a first-order reaction to go to 99% completion relate to the half-life of the reaction?

**Solution:**

From Table 9.1 we are given the following information,

1<sup>st</sup> order reaction:

$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}, \quad t_{1/2} = \frac{\ln 2}{k}$$

With this we know that after the half life, there is only 50 percent of the substance left. This means that the fraction undecomposed is equal to 0.5.

$$\text{At } t_{1/2}, \quad \frac{a_0 - x}{a_0} = 0.5 \text{ and } 0.5 = \exp(-kt_{1/2})$$

If the reaction goes to 99 percent completion, this would mean that the fraction undecomposed will be equal to 0.01 and therefore,

$$\text{At } t_{99}, \quad \frac{a_0 - x}{a_0} = 0.01 \text{ and } 0.01 = \exp(-kt_{99})$$

Let us now rearrange these expressions in order to isolate for the time variable.

$$\frac{1}{0.5} = \exp(kt_{1/2})$$

$$\ln 2 = \ln \exp(kt_{1/2})$$

$$t_{1/2} = \frac{\ln 2}{k}$$

$$\frac{1}{0.01} = \exp(kt_{99})$$

$$\ln 100 = \ln \exp(kt_{99})$$

$$t_{99} = \frac{\ln 100}{k}$$

Taking the ratio of these two expressions will show us how the time required for a first-order reaction to go to 99% completion relates to the half-life of the reaction.

$$\frac{t_{99}}{t_{1/2}} = \frac{\frac{\ln 100}{k}}{\frac{\ln 2}{k}} = \frac{\ln 100}{k'} \times \frac{k'}{\ln 2} = \frac{\ln 100}{\ln 2} \rightarrow \boxed{\frac{t_{99}}{t_{1/2}} = 6.64}$$

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- 9.6.** The rate constant for the reaction  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$  is  $1.3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate the half-life for the neutralization process if (a)  $[\text{H}^+] = [\text{OH}^-] = 10^{-1} \text{ M}$  and (b)  $[\text{H}^+] = [\text{OH}^-] = 10^{-4} \text{ M}$ .

**Solution:**

Given:  $k = 1.3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $[\text{H}^+] = [\text{OH}^-] = 10^{-1} \text{ M}$ ,  $[\text{H}^+] = [\text{OH}^-] = 10^{-4} \text{ M}$

Required:  $t_{1/2}$  in each case

We will again look at the rate constant in order to determine the overall order of the reaction. Since the units are  $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , from Table 9.1 we can see that the reaction is 2<sup>nd</sup> order.

- a)** The half life for the neutralization process  $[\text{H}^+] = [\text{OH}^-] = 10^{-1} \text{ M}$  is therefore,

$$t_{1/2} = \frac{1}{ka_0}$$

$$t_{1/2} = \frac{1}{(1.3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})(10^{-1} \text{ M})}$$

$$1 \text{ M} = 1 \text{ mol L}^{-1}$$

$$1 \text{ L} = 1 \text{ dm}^3$$

$$t_{1/2} = \frac{1}{(1.3 \times 10^{11} \cancel{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}})(10^{-1} \cancel{\text{mol dm}^{-3}})}$$

$$t_{1/2} = 7.7 \times 10^{-11} \text{ s}$$

- b)** The half life for the neutralization process  $[\text{H}^+] = [\text{OH}^-] = 10^{-4} \text{ M}$  is therefore,

$$t_{1/2} = \frac{1}{ka_0}$$

$$t_{1/2} = \frac{1}{(1.3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})(10^{-4} \text{ M})}$$

$$1 \text{ M} = 1 \text{ mol L}^{-1}$$

$$1 \text{ L} = 1 \text{ dm}^3$$

$$t_{1/2} = \frac{1}{(1.3 \times 10^{11} \cancel{\text{ dm}^3 \text{ mol}^{-1}} \text{ s}^{-1})(10^{-4} \cancel{\text{ mol dm}^{-3}})}$$

$$t_{1/2} = 7.7 \times 10^{-8} \text{ s}$$

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**9.7.** The isotope  $^{90}\text{Sr}$  emits radiation by a first-order process (as is always the case with radioactive decay) and has a half-life of 28.1 years. When ingested by mammals it becomes permanently incorporated in bone tissue. If  $1\ \mu\text{g}$  is absorbed at birth, how much of this isotope remains after (a) 25 years, (b) 50 years, (c) 70 years?

**Solution:**

Given:  $^{90}\text{Sr}$ :  $t_{1/2} = 28.1\ \text{years}$ ,  $m = 1\ \mu\text{g}$

Required: fraction remaining in each case

It is first important to determine the rate constant. Since we are told that the radioactive decay is a 1<sup>st</sup> order process, we can use Table 9.1 in order to calculate its value.

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}}$$

$$t_{1/2} = 28.1\ \text{yrs}$$

$$k = \frac{0.693147}{28.1\ \text{yrs}}$$

$$k = 0.024\ 667\ \text{yrs}^{-1}$$

Now we will use the integrated form in order to isolate for the fraction undecomposed after a certain period of time.

$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}$$

$$kt = \ln \frac{a_0}{a_0 - x}$$

$$\exp(kt) = \exp\left(\ln \frac{a_0}{a_0 - x}\right)$$

$$\exp(-kt) = \frac{a_0 - x}{a_0} = \text{fraction undecomposed}$$

a) After 25 years,

$$\frac{a_0 - x}{a_0} = \exp\left(-0.024\,667 \text{ yrs}^{-1} \times 25 \text{ yrs}\right)$$

$$\frac{a_0 - x}{a_0} = 0.540 \text{ }\mu\text{g}$$

0.540  $\mu\text{g}$  remain after 25 years

b) After 50 years

$$\frac{a_0 - x}{a_0} = \exp\left(-0.024\,667 \text{ yrs}^{-1} \times 50 \text{ yrs}\right)$$

$$\frac{a_0 - x}{a_0} = 0.291 \text{ }\mu\text{g}$$

0.291  $\mu\text{g}$  remain after 50 years

c) After 70 years,

$$\frac{a_0 - x}{a_0} = \exp\left(-0.024\,667 \text{ yrs}^{-1} \times 70 \text{ yrs}\right)$$

$$\frac{a_0 - x}{a_0} = 0.178 \text{ }\mu\text{g}$$

0.178  $\mu\text{g}$  remain after 70 years

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**9.8.** The first-order decomposition of nitramide in the presence of bases,  $\text{NH}_2\text{NO}_2 \rightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$ , is conveniently analyzed by collecting the gas evolved during the reaction. During an experiment, 50.0 mg of nitramide was allowed to decompose at 15 °C. The volume of dry gas evolved after 70.0 min. was measured to be 6.59 cm<sup>3</sup> at 1 bar pressure. Find the rate constant and the half-life for nitramide decomposition.

**Solution:**

Given: Nitramide:  $m = 50.0 \text{ mg}$ ,  $T = 15 \text{ °C}$ ,  $V = 6.59 \text{ cm}^3$ ,  $P = 1 \text{ bar}$ ,  $t = 70.0 \text{ min}$

Required:  $k, t_{1/2}$

When given this type of problem, it is essential that the number of moles of substance is found before the rate constant as well as the half life can be determined. Let us begin by using the Ideal Gas Law in order to do this.

$$PV = nRT$$

$$n_0 = \frac{m}{M} = \frac{50 \times 10^{-3} \cancel{\text{g}}}{62.023 \cancel{\text{g}} \text{ mol}^{-1}}$$

$$n_0 = 8.06 \times 10^{-4} \text{ mol}$$

$$n_{\text{reacted}}(70 \text{ min}) = \frac{PV}{RT}$$

$$n_{\text{reacted}}(70 \text{ min}) = \frac{(1 \cancel{\text{bar}})(6.59 \text{ cm}^3)}{(0.083145 \text{ dm}^3 \cancel{\text{bar}} \cancel{\text{K}}^{-1} \text{ mol}^{-1})(288 \cancel{\text{K}})}$$

$$1 \text{ cm}^3 = 0.001 \text{ dm}^3$$

$$n_{\text{reacted}}(70 \text{ min}) = \frac{6.59 \cancel{\text{cm}^3}}{23.94576 \cancel{\text{dm}^3} \text{ mol}^{-1}} \times \frac{0.001 \cancel{\text{dm}^3}}{1 \cancel{\text{cm}^3}}$$

$$n_{\text{reacted}}(70 \text{ min}) = 2.75 \times 10^{-4} \text{ mol}$$

Now that we have the initial number of moles and the number of moles reacted after 70 minutes, we can use this bit of information in the integrated rate law as the fraction of undecomposed substance.



$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x} = \frac{1}{t} \ln \frac{n_0}{n_0 - n_{\text{reacted}}}$$

$$k = \frac{1}{70 \text{ min}} \ln \frac{8.06 \times 10^{-4} \cancel{\text{mol}}}{(8.06 \times 10^{-4} - 2.75 \times 10^{-4}) \cancel{\text{mol}}}$$

$$\boxed{k = 5.96 \times 10^{-3} \text{ min}^{-1}}$$

The half life for the reaction may now be determined using the above value.

$$t_{1/2} = \frac{\ln 2}{k}$$

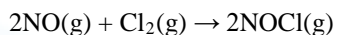
$$t_{1/2} = \frac{0.693147}{5.96 \times 10^{-3} \text{ min}^{-1}}$$

$$\boxed{t_{1/2} = 116 \text{ min}}$$

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**9.9.** The reaction:



is second order in NO and first order in  $\text{Cl}_2$ . In a volume of  $2 \text{ dm}^3$ , 5 mol of nitric oxide and 2 mol of  $\text{Cl}_2$  were brought together, and the initial rate was  $2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ . What will be the rate when one-half of the chlorine has reacted?

**Solution:**

Given:  $[\text{NO}]^2, [\text{Cl}_2]^1, V = 2 \text{ dm}^3, n_{\text{NO}} = 5 \text{ mol}, n_{\text{Cl}_2} = 2 \text{ mol}, k_0 = 2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$

Required:  $k$  when half of chlorine reacted

Let us first write out the rate law for this reaction (given that the reaction is second order in NO and first order in  $\text{Cl}_2$ ).

$$v = k [\text{NO}]^2 [\text{Cl}_2]^1$$

The easiest way to solve this problem is to construct a table which will enable us to examine the initial amounts of each species in addition to the amount after half of the chlorine is reacted.

	2NO	+	Cl <sub>2</sub>	→	2NOCl
initial	5		2		0 mol
reacted			1		
final	3		1		2 mol

The rate of reaction is therefore equal to:

$$rate_1 = k_1 [NO]^2 [Cl_2]^1$$

$$2.4 \times 10^{-3} = k_1 [5]^2 [2]^1$$

$$k_1 = \frac{2.4 \times 10^{-3}}{50} = 4.8 \times 10^{-5}$$

When one-half of the chlorine has reacted:

$$rate_2 = k_1 [3]^2 [1]^1$$

$$rate_2 = 4.8 \times 10^{-5} \times 9$$

$$rate_2 = 4.32 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

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**9.10.** Measuring the total pressure is a convenient way to monitor the gas phase reaction:



However, the rate depends on the concentration of the reactant, which is proportional to the partial pressure of the reactant. Derive an expression relating the rate of this reaction to the initial pressure,  $P_0$ , and the total pressure,  $P_t$ , at time  $t$ . Assume that the reaction follows second-order kinetics.

**Solution:**

Let us begin by mentioning that we will making reference to all quantities in terms of the number of moles. Let  $n_0$  denote the initial amount of NOCl and we will say that  $2x$  is the number of moles reacted after a period of time,  $t$ . We can again construct a table to facilitate our problem solving process.

	$2\text{NOCl(g)}$	$\rightarrow$	$2\text{NO(g)}$	$+$	$\text{Cl}_2\text{(g)}$
initial	$n_0$		0		0
reacted	$-2x$		$2x$		$x$
final	$n_0 - 2x$		$2x$		$x$

We can see that the total amount of gas at any given time ( $t$ ) is equal to:

$$n_0 - \cancel{2x} + \cancel{2x} + x = n_0 + x$$

With this information, we can now calculate the concentrations. We will make use of the Ideal Gas Law which states that,

$$PV = nRT$$

$$P_0 = \frac{n_0 RT}{V}$$

$$\text{initial concentration} \rightarrow \frac{n}{V}$$

$$\frac{n_0}{V} = \frac{P_0}{RT}$$

Let us now derive the expression for the concentration at the time  $t$ .

$$P_t = \overbrace{(n_0 + x)}^{\text{total number of moles}} \frac{RT}{V}$$

$$\frac{P_t}{RT} = \frac{n_0}{V} + \frac{x}{V}$$

$$\frac{x}{V} = \frac{P_t}{RT} - \frac{n_0}{V}$$

Substituting the original expression  $\frac{n_0}{V} = \frac{P_0}{RT}$  into the expression for the concentration at time  $t$ , we get,

$$\frac{x}{V} = \frac{P_t}{RT} - \frac{n_0}{V} = \frac{P_t}{RT} - \frac{P_0}{RT}$$

$$\frac{x}{V} = \frac{P_t - P_0}{RT} = [\text{Cl}]_2 = 2[\text{NO}]$$

And

$$\frac{n_0 - 2x}{V} = \frac{P_0}{RT} - \left( \frac{2P_t - 2P_0}{RT} \right) = \frac{3P_0 - 2P_t}{RT} = [\text{NOCl}]$$

$$\text{rate} = \frac{-d[\text{NOCl}]}{dt} = k[\text{NOCl}]^2 = \frac{k[3P_0 - 2P_t]^2}{R^2 T^2}$$

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**9.11.** The following results were obtained for the rate of decomposition of acetaldehyde:  
% decomposed:

0	5	10	15	20	25	30	35	40	45	50
Rate/Torr min <sup>-1</sup>										
8.53	7.49	6.74	5.90	5.14	4.69	4.31	3.75	3.11	2.67	2.29

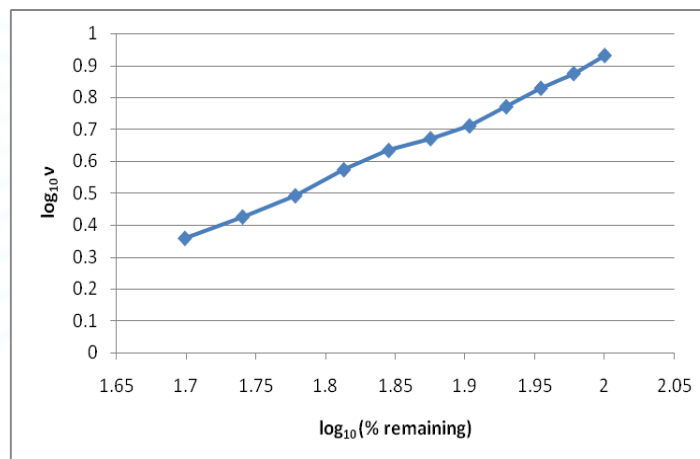
Employ van't Hoff's differential method to obtain the order of reaction.

**Solution:**

It is best to solve this type of problem using Microsoft Excel or any other math program that will enable you to plot this curve. Employing the Van't Hoff method, we obtain the following values:

% decomposed	v Torr min <sup>-1</sup>	log <sub>10</sub> (% remaining)	log <sub>10</sub> (v Torr min <sup>-1</sup> )
0	8.53	2.00	0.931
5	7.49	1.98	0.874
10	6.74	1.95	0.829
15	5.9	1.93	0.771
20	5.14	1.90	0.711
25	4.69	1.88	0.671
30	4.31	1.85	0.634
35	3.75	1.81	0.574
40	3.11	1.78	0.493
45	2.67	1.74	0.427
50	2.29	1.70	0.360

We can now plot log<sub>10</sub>(v/Torr min<sup>-1</sup>) versus log<sub>10</sub>(% remaining). The slope will then be the order of the reaction (with respect to time).



Using the slope function on Microsoft Excel we obtain,

slope = 1.865272965

slope = 2.0 to the nearest half integer

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**9.12.** The isotope  $^{32}_{15}\text{P}$  emits radiation and has a half-life of 14.3 days. Calculate the decay constant in  $\text{s}^{-1}$ . What percentage of the initial activity remains after (a) 10 days, (b) 20 days, (c) 100 days?

**Solution:**

Given:  $^{32}_{15}\text{P} : t_{1/2} = 14.3 \text{ days}$

Required: decay constant, percentage of initial activity

Let us begin by determining the rate constant. According to Table 9.1,

$$t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = 14.3 \text{ days} \times \frac{24 \text{ hrs}}{1 \text{ day}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}}$$

$$t_{1/2} = 1\,235\,520 \text{ s}$$

$$k = \frac{0.693\,147}{1\,235\,520 \text{ s}}$$

$$\boxed{k = 5.61 \times 10^{-7} \text{ s}^{-1}} \text{ or,}$$

$$k = \frac{0.693\,147}{14.3 \text{ days}}$$

$$k = 0.0485 \text{ days}^{-1}$$

**a)** Percentage of initial activity remaining after 10 days



$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}$$

$$kt = \ln \frac{a_0}{a_0 - x}$$

$$\exp(kt) = \cancel{\ln} e^{\left( \frac{a_0}{a_0 - x} \right)}$$

$$\exp(-kt) = \frac{a_0 - x}{a_0}$$

$$\frac{a_0 - x}{a_0} = \exp\left(-0.0485 \cancel{\text{ days}^{-1}} \times 10 \cancel{\text{ days}}\right)$$

$$\frac{a_0 - x}{a_0} = 0.615\,697 \times 100\%$$

62% active

**b)** Percentage of initial activity remaining after 20 days

$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}$$

$$kt = \ln \frac{a_0}{a_0 - x}$$

$$\exp(kt) = \cancel{\ln} e^{\left( \frac{a_0}{a_0 - x} \right)}$$

$$\exp(-kt) = \frac{a_0 - x}{a_0}$$

$$\frac{a_0 - x}{a_0} = \exp\left(-0.0485 \cancel{\text{ days}^{-1}} \times 20 \cancel{\text{ days}}\right)$$

$$\frac{a_0 - x}{a_0} = 0.379\,083 \times 100\%$$

38% active

c) Percentage of initial activity remaining after 100 days

$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}$$

$$kt = \ln \frac{a_0}{a_0 - x}$$

$$\exp(kt) = \cancel{\ln} e^{\left( \frac{a_0}{a_0 - x} \right)}$$

$$\exp(-kt) = \frac{a_0 - x}{a_0}$$

$$\frac{a_0 - x}{a_0} = \exp\left(-0.0485 \cancel{\text{ days}^{-1}} \times 100 \cancel{\text{ days}}\right)$$

$$\frac{a_0 - x}{a_0} = 0.007\,828 \times 100\%$$

0.78% active

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**9.13.** The following counts per minute were recorded on a counter for the isotope  $^{35}_{16}\text{S}$  at various times:

Time/d	Counts/min
0	4280
1	4245
2	4212
3	4179
4	4146
5	4113
10	3952
15	3798

Determine the half-life in days and the decay constant in  $\text{s}^{-1}$ . How many counts per minute would be expected after (a) 60 days and (b) 365 days?

**Solution:**

Given:  $^{35}_{16}\text{S}$ : see above

Required:  $t_{1/2}$ , decay constant in each case

In order to plot this graph, we will use roughly the same method as we did in problem 9.11.

t (days)	n (min)	$\ln(n_0/n)$
0	4280	0.00E+00
1	4245	8.21E-03
2	4212	1.60E-02
3	4179	2.39E-02
4	4146	3.18E-02
5	4113	3.98E-02
10	3952	7.97E-02
15	3798	1.19E-01

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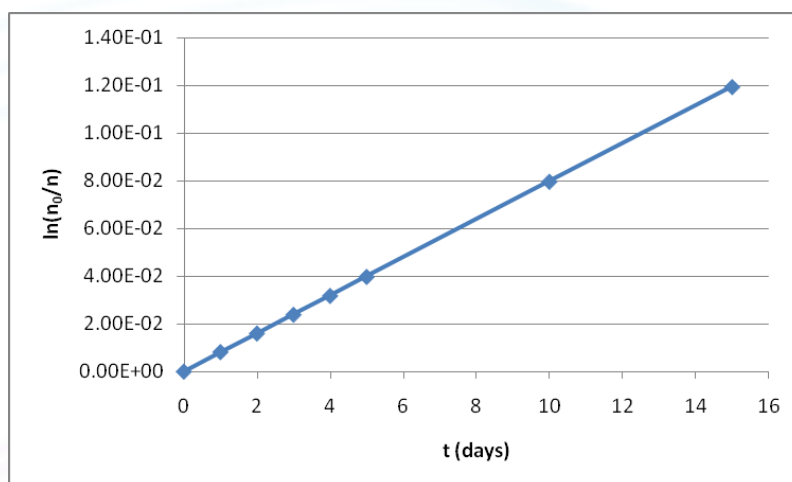
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We can plot  $\ln(n_0/n)$  against  $t$  in order to find the slope,  $k$ . It is equally possible to simply calculate the slope based on the rise over run principle.

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{0.119}{15} = 7.93 \times 10^{-3} \text{ days}^{-1}$$

$$k = 7.93 \times 10^{-3} \text{ days}^{-1} \rightarrow \boxed{k = 9.18 \times 10^{-8} \text{ s}^{-1}}$$



This plot indicates that the reaction is first order.

Now that we have determined the value of the decay constant, we can find the half life.

$$t_{1/2} = \frac{0.693}{7.93 \times 10^{-3} \text{ days}^{-1}}$$

$$\boxed{t_{1/2} = 87 \text{ days}}$$

- a) The number of counts per minute expected after 60 days,

$$\ln \frac{n_0}{n(t)} = kt = \left( \frac{0.693}{87} \right) t$$

$$kt_{60} = \left( 7.93 \times 10^{-3} \text{ days}^{-1} \right) (60 \text{ days})$$

$$kt_{60} = 0.4758 = \ln \frac{n_0}{n}$$

$$\exp(0.4758) = \cancel{\ln} e^{\frac{n_0}{n}}$$

$$\frac{n_0}{n} = 1.609\,301$$

$$n = \frac{n_0}{1.609\,301} = \frac{4280}{1.609\,301} = 2659.5$$

$$\boxed{n = 2660 \text{ counts}}$$

b) The number of counts per minute expected after 365 days,

$$kt_{60} = \left( 7.93 \times 10^{-3} \text{ days}^{-1} \right) (365 \text{ days})$$

$$kt_{60} = 2.894\,45 = \ln \frac{n_0}{n}$$

$$\exp(2.894\,45) = \cancel{\ln} e^{\frac{n_0}{n}}$$

$$\frac{n_0}{n} = 18.073\,558$$

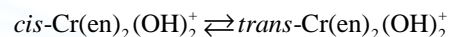
$$n = \frac{n_0}{18.073\,558} = \frac{4280}{18.073\,558} = 236.8$$

$$\boxed{n = 237 \text{ counts}}$$

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**9.14.** The reaction:



is first order in both directions. At 25 °C the equilibrium constant is 0.16 and the rate constant  $k_1$  is  $3.3 \times 10^{-4} \text{ s}^{-1}$ . In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed?

**Solution:**

Given:  $T = 25 \text{ °C}$ ,  $k_{\text{eq}} = 0.16$ ,  $k_1 = 3.3 \times 10^{-4} \text{ s}^{-1}$

Required: see above

It is important to realize that these are two opposing reactions occurring at the same time. We are told that they are 1<sup>st</sup> order in both directions therefore for the reaction  $A \xrightleftharpoons[k_{-1}]{k_1} Z$ , if the experiment is starting with the pure *cis* form of the isomer of concentration  $a_0$  and if after time  $t$ , the concentration of the *trans* form of the isomer has the concentration  $x$ , then that of the *cis* form will be equal to  $a_0 - x$ .

If the forward reaction were to occur in isolation, it's rate equation could be written as;

$$v_1 = k_1(a_0 - x)$$

While the rate of the reverse reaction would be written as;

$$v_{-1} = k_{-1}x$$

Since these reactions are in opposite directions, we can define the net rate of change of concentration of the *trans* isomer as:

$$\frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x$$

If  $x_e$  is the concentration of the *trans* isomer at equilibrium (this is when the net rate is zero), then we know that,

$$k_1(a_0 - x) - k_{-1}x = 0$$

$$k_1(a_0 - x) = k_{-1}x$$

$$\frac{k_1}{k_{-1}} = k_{\text{eq}} = \frac{x_e}{(a_0 - x_e)}$$

It is possible to eliminate  $k_{-1}$  in order to obtain the following Eq. 9.47:

$$\frac{dx}{dt} = \frac{k_1 a_0}{x_e} (x_e - x)$$

Integration of this equation, subject to the boundary condition that  $x = 0$  when  $t = 0$  gives the rate equation corresponding to Eq. 9.48:

$$k_1 t = \frac{x_e}{a_0} \ln \frac{x_e}{(x_e - x)} \quad \text{or} \quad \frac{a_0 k_1 t}{x_e} = \ln x_e - \ln (x_e - x)$$

For half of the equilibrium amount of product to be formed, it would mean that  $x = \frac{x_e}{2}$ . Making this substitution into the above will yield,

$$k_1 t_{1/2} = \frac{x_e}{a_0} \ln \frac{x_e}{\left(x_e - \frac{x_e}{2}\right)}$$

$$k_1 t_{1/2} = \frac{x_e}{a_0} \ln \frac{x_e}{\left(\frac{x_e}{2}\right)}$$

$$k_1 t_{1/2} = \frac{x_e}{a_0} \ln \left( \cancel{x_e} \times \frac{2}{\cancel{x_e}} \right)$$

$$k_1 t_{1/2} = \frac{x_e}{a_0} \ln 2$$

Having been given the equilibrium constant as well as the rate constant for the forward reaction, we can now do a few more calculations in order to determine how long it would take for half the equilibrium amount of the *trans* isomer to be formed.



$$k_{\text{eq}} = \frac{x_e}{(a_0 - x_e)} = 0.16$$

$$\frac{1}{k_{\text{eq}}} = \frac{(a_0 - x_e)}{x_e} = \frac{1}{0.16}$$

$$\frac{(a_0 - x_e)}{x_e} = \frac{a_0}{x_e} - 1 = \frac{1}{0.16}$$

$$\frac{a_0}{x_e} = 1 + \frac{1}{0.16}$$

$$\frac{a_0}{x_e} = 7.25$$

$$k_1 t_{1/2} = \frac{x_e}{a_0} \ln 2$$

$$t_{1/2} = \frac{\frac{x_e}{a_0} \ln 2}{k_1} = \frac{\ln 2}{\frac{a_0}{x_e} k_1}$$

$$t_{1/2} = \frac{0.693147}{(7.25 \times 3.3 \times 10^{-4} \text{ s}^{-1})}$$

$$t_{1/2} = 289.7 \text{ s}$$

$$\boxed{t_{1/2} = 290 \text{ s}}$$

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**9.15.** Suppose that a gas phase reaction  $2A(g) \rightarrow 2B(g) + C(g)$  follows second-order kinetics and goes to completion. If the reaction is allowed to proceed in a constant volume vessel at an initial pressure of 2 bar (only A is initially present), what will be the partial pressures of A, B, and C and the total pressure at  $t = t_{1/2}$ ,  $2t_{1/2}$ ,  $3t_{1/2}$ , and infinity?

**Solution:**

Given:  $2A(g) \rightarrow 2B(g) + C(g)$  (second order),  $P_0 = 2$  bar

Required:  $P_A, P_B, P_C, P_{\text{tot}}$  at  $t = t_{1/2}, 2t_{1/2}, 3t_{1/2}$  and infinity

Recall from section 9.4 that if we have a reaction of either of the following forms:



We can write the rate equation in its differential form according to Eq. 9.31 and Eq. 9.32.

$$\frac{dx}{dt} = k(a_0 - x)^2$$

$$kdt = \frac{dx}{(a_0 - x)^2}$$

Eq. 9.32 can then be integrated in order to obtain the following:

$$kt + I = \frac{1}{(a_0 - x)}$$

$I$  = constant of integration

when  $x = 0, t = 0$

$$I = \frac{1}{(a_0)}$$

$$kt = \frac{x}{a_0(a_0 - x)} \rightarrow kt = \frac{1}{a_0 - 2x} - \frac{1}{(a_0)}$$

Let us assume that  $2x$  moles of substance A are consumed in each step. For a 2<sup>nd</sup> order reaction, we can check Table 9.1 or look at Eq. 9.40 in order to find the expression for the half life.

$$t_{1/2} = \frac{1}{(a_0)k}$$

Since all of the times asked for are written in multiples of the half life, we can write,

$$kt = \frac{n}{a_0} = \frac{1}{a_0 - 2x} - \frac{1}{(a_0)} \text{ where } n = 1, 2, 3, \infty$$

Further simplification of this expression gives,

$$\frac{n}{a_0} + \frac{1}{(a_0)} = \frac{1}{a_0 - 2x}$$

$$\frac{n+1}{a_0} = \frac{1}{a_0 - 2x}$$

$$\frac{a_0}{n+1} = a_0 - 2x$$

$$2x = a_0 - \frac{a_0}{n+1}$$

$$x = \frac{a_0}{2} \left( \frac{n}{n+1} \right)$$

Using simple stoichiometry, we can see that,

$$P_A \propto a_0 - 2x$$

$$P_B \propto 2x$$

$$P_C \propto x$$

Since  $\frac{a_0}{n+1} = a_0 - 2x$ , then

$$P_A = \frac{P_0}{n+1}$$

Since  $2x = a_0 - \frac{a_0}{n+1}$  then

$$P_B = P_0 \frac{n}{n+1}$$

Since  $x = \frac{a_0}{2} \left( \frac{n}{n+1} \right)$  then

$$P_C = \frac{P_0}{2} \left( \frac{n}{n+1} \right)$$

Using the above three expressions, we can construct a table which will give the partial pressures for each species in addition to the total pressure at each temperature.

t	P <sub>A</sub> (bar)	P <sub>B</sub> (bar)	P <sub>C</sub> (bar)	P <sub>tot</sub> (bar)
t <sub>0</sub>	2.000	0.000	0.000	2.000
t <sub>1/2</sub>	1.000	1.000	0.500	2.500
2t <sub>1/2</sub>	0.667	1.333	0.667	2.667
3t <sub>1/2</sub>	0.500	1.500	0.750	2.750
t <sub>infinity</sub>	0.000	2.000	1.000	3.000

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**9.16.** Derive the following relationship for the half-life  $t_{1/2}$  of a reaction of order  $n$ , with all reactants having an initial concentration  $a_0$ :

$$t_{1/2} = \frac{2^{n-1} - 1}{ka_0^{n-1} (n-1)}$$

**Solution:**

From Table 9.1, we are given the general expression for a reaction of the  $n^{\text{th}}$  order. We can separate the variables and integrate this in order to generate the above equation for the half life of an  $n^{\text{th}}$  order reaction.

$$\frac{dx}{dt} = k(a_0 - x)^n$$

$$kdt = \frac{dx}{(a_0 - x)^n}$$

$$\int kdt = \int \frac{dx}{(a_0 - x)^n}$$

$$kt = \frac{(a_0 - x)^{1-n}}{(n-1)}$$

$$k = \frac{1}{t(n-1)} \left[ \frac{1}{(a_0 - x)^{n-1}} - \frac{1}{a_0^{n-1}} \right]$$

Recall that at the half life,  $x = \frac{a_0}{2}$  and therefore,

$$k = \frac{1}{t_{1/2}(n-1)} \left[ \frac{1}{\left(a_0 - \frac{a_0}{2}\right)^{n-1}} - \frac{1}{a_0^{n-1}} \right]$$

$$k = \frac{1}{t_{1/2}(n-1)} \left[ \frac{1}{\left(\frac{a_0}{2}\right)^{n-1}} - \frac{1}{a_0^{n-1}} \right]$$

$$t_{1/2} = \frac{1}{k(n-1)} \left[ \frac{1}{\left(\frac{a_0}{2}\right)^{n-1}} - \frac{1}{a_0^{n-1}} \right]$$

Further simplification will yield,

$$t_{1/2} = \frac{1}{k(n-1)} \left[ \left(\frac{a_0}{2}\right)^{1-n} - a_0^{1-n} \right]$$

$$\left[ \left(\frac{a_0}{2}\right)^{1-n} - a_0^{1-n} \right] = a_0^{1-n} 2^{n-1} - a_0^{1-n} = a_0^{1-n} (2^{n-1} - 1)$$

$$t_{1/2} = \frac{(2^{n-1} - 1)}{ka_0^{n-1}(n-1)}$$

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**9.17.** Vaughan [*J. Am. Chem. Soc.* 54, 3867(1932)] reported the following pressure measurements as a function of time for the dimerization of 1,3-butadiene ( $C_4H_6$ ) under constant volume conditions at 326 °C:

$t/\text{min}$	3.25	12.18	24.55	42.50	68.05
$P/\text{Torr}$	618.5	584.2	546.8	509.3	474.6

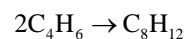
The initial amount of butadiene taken would have exerted a pressure of 632.0 Torr. Find whether the reaction follows first- or second-order kinetics and evaluate the rate constant.

**Solution:**

Given: see above

Required: first or second order kinetics?  $k$

First we should write out the balanced reaction for this process.



initial	$n_0$	0
time $t$	$n_0 - 2x$	$x$

We are again assuming that  $2x$  moles are being consumed in each step (problem 9.15). From this, we can determine the number of moles at any given time,  $t$ .

$$n_0 - 2x + x = n_0 - x$$

$$n_0 - x \text{ at time } t$$

Using the Ideal Gas Law, we can derive expressions for the number of moles in both instances.



$$PV = nRT$$

$$P_0 = \frac{n_0 RT}{V}$$

$$P_t = \frac{(n_0 - x) RT}{V}$$

$$P_0 - P_t = \frac{n_0 RT}{V} - \frac{(n_0 - x) RT}{V}$$

$$P_0 - P_t = \frac{RT}{V} [P_0 - (P_0 - x)]$$

$$P_0 - P_t = \frac{xRT}{V}$$

The partial pressure of butadiene at a time  $t$ , can therefore be expressed as,

$$P_{\text{C}_4\text{H}_6} = 2P_t - P_0 = \frac{(n_0 - 2x) RT}{V}$$

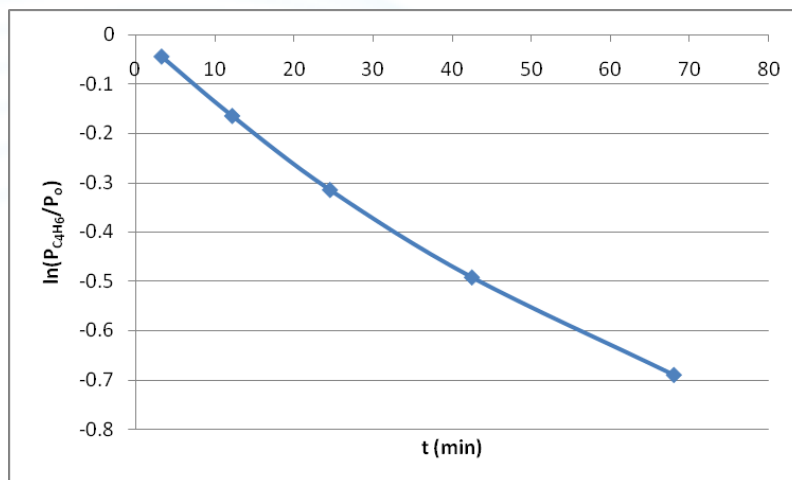
e.g. at time 3.25min,  $P_t = 618.5$  Torr

$$P_{\text{C}_4\text{H}_6}(3.25) = 2 \times 618.5 - 632 = 605 \text{ etc.}$$

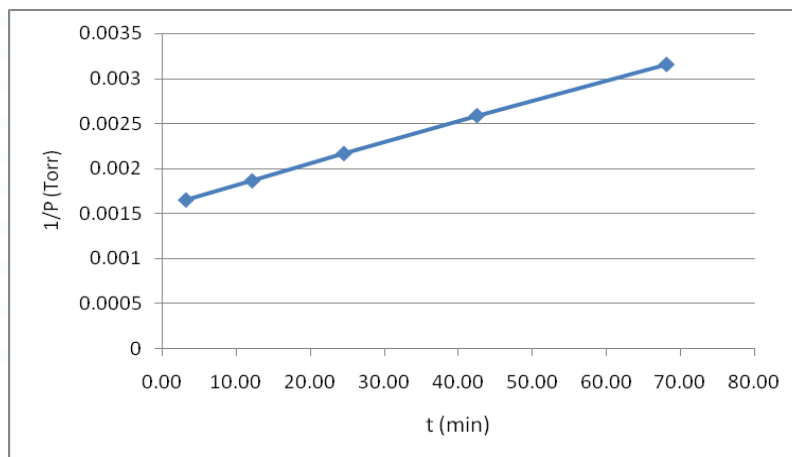
Re-tabulating the given data in terms of the partial pressure of butadiene will yield,

$t/\text{min}$	3.25	12.18	24.55	42.50	68.05
$P_{\text{C}_4\text{H}_6}/\text{Torr} = 2P_t - P_o$	605.0	536.4	461.6	386.6	317.2
$\ln\left(\frac{P_{\text{C}_4\text{H}_6}}{P_o}\right)$	-0.0437	-0.1640	-0.3142	-0.4915	-0.6894

In order to determine whether the reaction proceeds according to 1<sup>st</sup> or 2<sup>nd</sup> order kinetics, one should first plot  $P_{\text{C}_4\text{H}_6}$  vs.  $t$ . This plot yields curved line.



This means that the reaction does NOT proceed according to 1<sup>st</sup> order kinetics and therefore, we must now try to plot the inverse of the pressure versus time.



This straight-line plot indicates that the reaction follows 2<sup>nd</sup> order kinetics. It is also possible to perform a linear regression (using Microsoft Excel Linest Function) in order to reveal the integrated rate law.

2<sup>nd</sup> order kinetics

linear regression statistics:

2.31869E-05	0.001586
2.66985E-07	1.01E-05
0.999602407	1.38E-05
7542.405387	3

$$\frac{1}{P_{\text{C}_4\text{H}_6}} = 2.31869 \times 10^{-5} t + 0.001586$$

Remember that the slope of this line will be equal to the rate constant,  $k$ .

$$k = 2.31869 \times 10^{-5}$$

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- 9.18.** A drug administered to a patient is usually consumed by a first-order process. Suppose that a drug is administered in equal amounts at regular intervals and that the interval between successive doses is equal to the  $(1/n)$ -life for the disappearance process (i.e., to the time that it takes for the fraction  $1/n$  to disappear). Prove that the limiting concentration of the drug in the patient's body is equal to  $n$  times the concentration produced by an individual dose.

**Solution:**

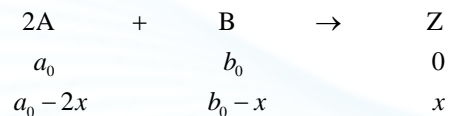
When the concentration has reached  $nc$ , where  $c$  is the concentration produced by a single dose, the concentration will fall to  $(n-1)c$  during the interval between successive doses. The next dose restores the concentration to  $(n-1)c + c$  which when simplified is equal to  $nc$ . This indicates that the steady state has been reached.

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**9.19.** Equation 9.45 applies to a second-order reaction of stoichiometry  $A + B \rightarrow Z$ . Derive the corresponding equation for a second-order reaction of stoichiometry  $2A + B \rightarrow Z$ .

**Solution:**



$$\frac{dx}{dt} = k(a_0 - 2x)(b_0 - x)$$

$$kdt = \frac{dx}{(a_0 - 2x)(b_0 - x)}$$

$$kdt = \frac{dx}{(a_0 - 2x)(b_0 - x)} = \left[ \frac{1}{(a_0 - 2x)} - \frac{1}{2(b_0 - x)} \right] \frac{dx}{2b_0 - a_0}$$

$$\int kdt = \int \left[ \frac{1}{(a_0 - 2x)} - \frac{1}{2(b_0 - x)} \right] \frac{dx}{2b_0 - a_0}$$

$$kt = \frac{1}{2b_0 - a_0} \left[ -\frac{1}{2} \ln(a_0 - 2x) + \frac{1}{2} \ln 2(b_0 - x) \right] + I$$

when  $x = 0, t = 0$

$$I = \frac{1}{2b_0 - a_0} \left[ -\frac{1}{2} \ln(a_0 - \cancel{2x}) + \frac{1}{2} \ln 2(b_0 - \cancel{x}) \right]$$

$$kt = \frac{1}{2b_0 - a_0} \left[ \frac{1}{2} \ln \frac{a_0}{(a_0 - 2x)} - \frac{1}{2} \ln \frac{\cancel{2}b_0}{\cancel{2}(b_0 - x)} \right]$$

$$\boxed{kt = \frac{1}{2(2b_0 - a_0)} \ln \frac{a_0(b_0 - x)}{b_0(a_0 - 2x)}}$$

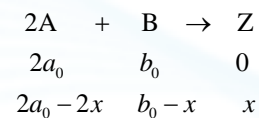
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**9.20.** Derive the integrated rate equation for an irreversible reaction of stoichiometry  $2A + B \rightarrow Z$ , the rate being proportional to  $[A]^2[B]$  and the reactants present in stoichiometric proportions; take the initial concentration of A as  $2a_0$  and that of B as  $a_0$ . Obtain an expression for the half-life of the reaction.

**Solution:**



$$v = k[A]^2[B]$$

$$[A]_0 = 2a_0$$

$$[B]_0 = b_0$$

$$\frac{dx}{dt} = k(2a_0 - 2x)^2(b_0 - x)$$

For simplicity, we will say that  $(b_0 - x) = (a_0 - x)$ . Making this substitution into the above yield,



$$(2a_0 - 2x)^2 = (2a_0 - 2x)(2a_0 - 2x)$$

$$(2a_0 - 2x)^2 = 4a_0^2 - 4a_0x - 4a_0x + 4x^2 = 4(a_0^2 - 2a_0x + x^2)$$

$$(2a_0 - 2x)^2 = 4(a_0 - x)^2$$

$$\frac{dx}{dt} = 4k(a_0 - x)^2$$

$$4kdt = \frac{dx}{(a_0 - x)^2}$$

$$4 \int kdt = \int \frac{dx}{(a_0 - x)^2}$$

$$4kt + I = \frac{1}{2(a_0 - x)^2}$$

$$\text{when } x = 0, t = 0$$

$$I = \frac{1}{2(a_0 - \cancel{x})^2} = \frac{1}{2a_0^2}$$

$$4kt = \frac{1}{2(a_0 - x)^2} - \frac{1}{2a_0^2}$$

$$\text{at } t_{1/2}, x = \frac{a_0}{2} \text{ hence,}$$

$$4kt_{1/2} = \frac{1}{2\left(a_0 - \frac{a_0}{2}\right)^2} - \frac{1}{2a_0^2} = \frac{1}{2\left(\frac{a_0}{2}\right)^2} - \frac{1}{2a_0^2}$$

$$4kt_{1/2} = \frac{1}{\frac{a_0^2}{2}} - \frac{1}{2a_0^2} = \frac{2}{a_0^2} - \frac{1}{2a_0^2} = \frac{4}{2a_0^2} - \frac{1}{2a_0^2}$$

$$4kt_{1/2} = \frac{3}{2a_0^2}$$

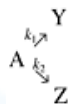
$$t_{1/2} = \frac{\frac{3}{2a_0^2}}{4k} = \frac{3}{2a_0^2} \times \frac{1}{4k}$$

$$\boxed{t_{1/2} = \frac{3}{8ka_0^2}}$$

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**9.21.** Prove that for two simultaneous (parallel) reactions



$$\frac{[\text{Y}]}{[\text{Z}]} = \frac{k_1}{k_2} \text{ at all times.}$$

**Solution:**

Let us begin by writing out the rate equations for each individual reaction.

$$\frac{d[\text{Y}]}{dt} = k_1 [\text{A}] \quad \text{and} \quad \frac{d[\text{Z}]}{dt} = k_2 [\text{A}]$$

Setting these expressions equal to one another it is possible to eliminate the concentration of A.

$$\frac{d[\text{Y}]}{dt} = k_1 [\cancel{\text{A}}] = \frac{d[\text{Z}]}{dt} = k_2 [\cancel{\text{A}}]$$

$$\frac{k_1}{k_2} = \frac{d[\text{Y}]}{d[\text{Z}]}$$

Integrate both sides of the equation to obtain,

$$\int \frac{k_1}{k_2} d[\text{Z}] = \int d[\text{Y}]$$

$$\frac{k_1}{k_2} [\text{Z}] + I = [\text{Y}]$$

Note that under the boundary condition  $t = 0$ , then  $[\text{Y}] = [\text{Z}]$  therefore,  $I = 0$  hence;

$$\frac{k_1}{k_2}[Z] + I = [Y]$$

$$I = 0$$

$$\frac{k_1}{k_2}[Z] + 0 = [Y]$$

$$\boxed{\frac{k_1}{k_2} = \frac{[Y]}{[Z]}}$$

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\*9.22. Prove that for two consecutive first-order reactions;  $A \rightarrow B \rightarrow C$  the rate of formation of C is given by:

$$[C] = [A]_0 \left( 1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} \right)$$

where  $[A]_0$  is the initial concentration of A.

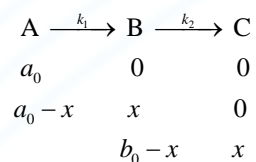
(Hint: The solution of the differential equation):

$$\frac{dx}{dt} = a b e^{-bt} - cx$$

where  $a$ ,  $b$ , and  $c$  are constants, is

$$x = \frac{ab}{c-b} (e^{-bt} - e^{-ct}) + I$$

**Solution:**



Writing out the rates of consumption and formation for each species, we will obtain,

$$\frac{-d[A]}{dt} = k_1 [A]$$

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B]$$

$$\frac{d[C]}{dt} = k_2 [B]$$

Let us integrate the first expression after separating the variables.

$$\int_{A_0}^{A_t} \frac{-d[A]}{[A]} = \int k_1 dt$$

$$\ln[A]_{A_0}^{A_t} = k_1 t$$

$$\ln[A]_t - \ln[A]_0 = k_1 t$$

$$\ln \frac{[A]_t}{[A]_0} = k_1 t$$

$$\ln \frac{[A]_t}{[A]_0} = \exp(-k_1 t)$$

$$[A]_t = [A]_0 \exp(-k_1 t)$$

This expression can be substituted into the rate of formation for substance B. This will yield,

$$\frac{d[B]}{dt} = k_1 [A]_0 \exp(-k_1 t) - k_2 [B]$$

With the boundary condition  $t = 0$ , this means that  $[B] = 0$  which allows us to further simplify the above.

$$\frac{d[B]}{dt} = k_1 [A]_0 \exp(-k_1 t) - k_2 [B] = 0$$

$$k_1 [A]_0 \exp(-k_1 t) = k_2 [B]$$

$$[B] = \frac{k_1 [A]_0 \exp(-k_1 t)}{k_2} \text{ and integrate to obtain,}$$

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} (e^{(-k_1 t)} - e^{(-k_2 t)})$$

$$[A]_0 = [A] + [B] + [C]$$

$$[C] = [A]_0 - [A] - [B]$$

$$[C] = [A]_0 - [A]_0 \exp(-k_1 t) - [A]_0 \frac{k_1}{k_2 - k_1} \left( e^{(-k_1 t)} - e^{(-k_2 t)} \right)$$

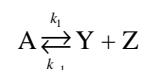
Simplify by method of factoring the above to get the appropriate expression (that which is sought after).

$$[C] = [A]_0 \left( 1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} \right)$$

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**\*9.23. a.** Derive the integrated rate equation for a reversible reaction of stoichiometry:



The reaction is first order from left to right and second order from right to left. Take the initial concentration of A as  $a_0$  and the concentration at time  $t$  as  $a_0 - x$ .

**b.** Obtain the integrated equation in terms of  $k$ , and the equilibrium constant  $K = k_1/k_{-1}$ .

**c.** A reaction to which this rate equation applies is the hydrolysis of methyl acetate. Newling and Hinshelwood, *J. Chem. Soc.*, 1936, 1357(1936), obtained the following results for the hydrolysis of 0.05 M ester at 80.2 °C in the presence of 0.05 M HCl, which catalyzes the reaction:

Time, s	1350	2070	3060	5340	7740	$\infty$
Percent hydrolysis	21.2	30.7	43.4	59.5	73.45	90.0

Obtain values for the rate constants  $k_1$  and  $k_{-1}$ .

**Solution:**

	A	$\xrightleftharpoons[k_{-1}]{k_1}$	Y	+	Z
initial	$a_0$		0		0
time $t$	$a_0 - x$		$x$		$x$

**a)** We can write out the rate equation with respect to the rate of consumption of the concentration of A.

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[Y][Z]$$

At a time  $t$ , this can then be written in the following form:

$$\frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x^2$$

Recall that at equilibrium,  $\frac{dx}{dt} = 0$  therefore,



$$\begin{aligned}
 k_1(a_0 - x_e) - k_{-1}x_e^2 &= 0 \\
 k_1(a_0 - x_e) &= k_{-1}x_e^2 \\
 k_{-1} &= \frac{k_1(a_0 - x_e)}{x_e^2} \quad (\dagger)
 \end{aligned}$$

Insertion of this expression into the first equation yields,

$$\begin{aligned}
 \frac{dx}{dt} &= k_1(a_0 - x) - \left( \frac{k_1(a_0 - x_e)}{\cancel{x_e^2}} \right) x^2 \\
 \frac{x_e^2 dx}{dt} &= x_e^2 k_1(a_0 - x) - x_e^2 k_1(a_0 - x_e) x^2 \\
 \frac{x_e^2 dx}{dt} &= k_1 \left[ x_e^2(a_0 - x) - x_e^2(a_0 - x_e)x^2 \right] \\
 \frac{x_e^2 dx}{\left[ x_e^2(a_0 - x) - x_e^2(a_0 - x_e)x^2 \right]} &= k_1 dt
 \end{aligned}$$

Integration of the LHS of this expression can be carried out after resolution into partial fractions.

$$\begin{aligned}
 \text{LHS} &= \frac{p}{a_0 - x} + \frac{q}{a_0 x_e + a_0 x - x_e x} \\
 p &= \frac{x_e}{2a_0 - x_e} \quad \text{and} \quad q = \frac{x_e(a_0 - x_e)}{2a_0 - x_e}
 \end{aligned}$$

The integration is now straightforward although rather lengthy. We will use the boundary conditions  $t = 0, x = 0$  which gives the following result.

$$k_1 = \frac{x_e}{(2a_0 - x_e)t} \ln \frac{a_0 x_e + x(a_0 - x_e)}{a_0(x_e - x)} \quad (*)$$

Readers wishing further mathematical details/explanation are referred to C. Capellos and B.H.T Bielski, *Kinetic Systems* (New York: Wiley, Interscience, 1972) pp.41-43.

b) Knowing that the equilibrium constant is  $K = k_1/k_{-1}$ , we may also write, from (†)

$$\begin{aligned} k_1(a_0 - x_e) - k_{-1}x_e^2 &= 0 \\ \frac{k_1(a_0 - x_e)}{k_{-1}} &= \frac{\cancel{k_{-1}}x_e^2}{\cancel{k_{-1}}} \\ \frac{k_1(\cancel{a_0 - x_e})}{k_{-1}(\cancel{a_0 - x_e})} &= \frac{x_e^2}{(a_0 - x_e)} \\ K = \frac{k_1}{k_{-1}} &= \frac{x_e^2}{(a_0 - x_e)} \end{aligned}$$

c) In order to deal with the numerical data which are in terms of percent hydrolysis, it is convenient to define,

$$r \equiv \frac{x}{a_0} \quad \text{and} \quad r_e \equiv \frac{x_e}{a_0}$$

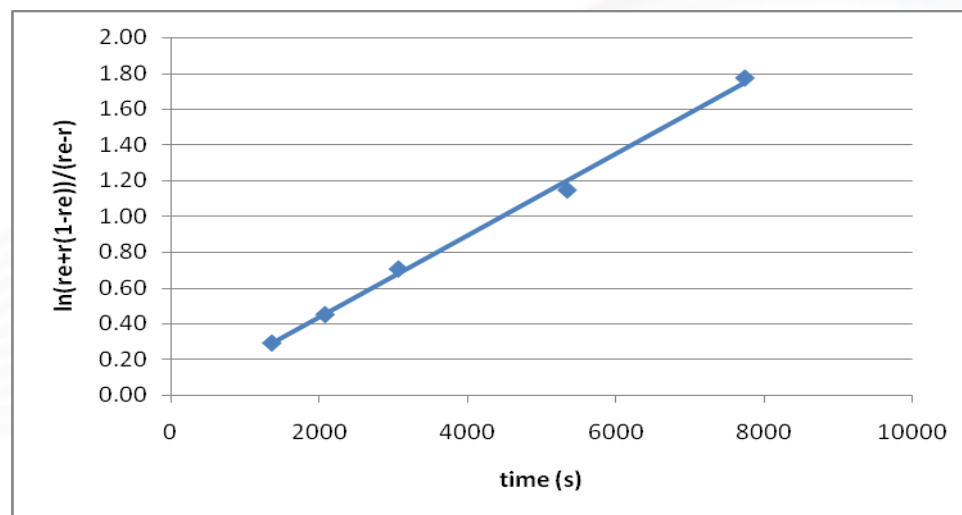
Substituting this into the integrated rate law derived in part A, (\*)

$$k_1 = \frac{r_e}{(2 - r_e)t} \ln \frac{r_e + r(1 - r_e)}{(r_e - r)}$$

From the data given in the problem, we have  $r_e = 0.90$ . We may now construct a table which will allow us to plot  $\ln \frac{r_e + r(1-r_e)}{(r_e - r)}$  versus time. Remember that the slope of this line will enable us to find the forward and reverse rate constant values.

$$\ln \left[ \frac{r_e + r(1-r_e)}{(r_e - r)} \right] = t \underbrace{\left( \frac{k_1(2-r_e)}{r_e} \right)}_{\text{slope}}$$

time (s)	r	$r_e + r(1-r_e)$	$r_e - r$	$\ln(r_e + r(1-r_e))/(r_e - r)$
1350	0.212	0.9212	0.688	0.2919
2070	0.307	0.9307	0.593	0.4507
3060	0.434	0.9434	0.466	0.7053
5340	0.595	0.9595	0.305	1.1461
7740	0.7345	0.97345	0.1655	1.7719



$$\text{slope} = \frac{1.64 - 0.35}{7000 \text{ s}} = 1.843 \times 10^{-4} \text{ s}^{-1} = \frac{k_1(2-r_e)}{r_e}$$

Solving for  $k_1$  we obtain,

$$\frac{k_1(2-r_e)}{r_e} = k_1 \frac{(2-0.90)}{0.90}$$

$$\frac{k_1(2-r_e)}{r_e} = 1.222k_1 = 1.843 \times 10^{-4} \text{ s}^{-1}$$

$$k_1 = \frac{1.843 \times 10^{-4} \text{ s}^{-1}}{1.222}$$

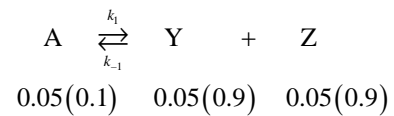
$$\boxed{k_1 = 1.51 \times 10^{-4} \text{ s}^{-1}}$$

This is done at constant catalyst concentration of 0.05 M HCl and makes  $k_1[0.05]$  1<sup>st</sup> order. The 2<sup>nd</sup> order rate constant is therefore,

$$k_1 = 1.51 \times 10^{-4} \text{ s}^{-1} \times \frac{1}{0.05 \text{ mol dm}^{-3}}$$

$$\boxed{k_1(2^{\text{nd}} \text{ order}) = 3.02 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

At equilibrium,



$$K = \frac{k_1}{k_{-1}} = \frac{[Y][Z]}{[A]} = \frac{(0.05(0.9))^2}{0.05(0.1)}$$

$$K = 0.405 \text{ mol dm}^{-3}$$

$$k_{-1} = \frac{k_1}{K} = \frac{1.51 \times 10^{-4} \text{ s}^{-1}}{0.405 \text{ mol dm}^{-3}}$$

$$\boxed{k_{-1} = 3.73 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

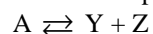
$$k_{-1} (2^{\text{nd}} \text{ order}) = 3.73 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \times \frac{1}{0.05 \text{ mol dm}^{-3}}$$

$$\boxed{k_{-1} (2^{\text{nd}} \text{ order}) = 7.46 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}}$$

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\*9.24. The dissociation of a weak acid  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$  can be represented as:



The rate constants  $k_1$  and  $k_{-1}$  cannot be measured by conventional methods but can be measured by the T-jump technique (Section 9.5). Prove that the relaxation time is given by:

$$t^* = \frac{1}{k_1 + 2k_{-1}x_e}$$

where the concentration of the ions (Y and Z) is at equilibrium.

**Solution:**

If  $a_0$  is the initial concentration of substance A and  $x$  is the concentration of ions at equilibrium, then the corresponding rate law is the same one as we have seen in the previous problem.

$$\frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x^2$$

At equilibrium,  $\frac{dx}{dt} = 0$

$$k_1(a_0 - x_e) - k_{-1}x_e^2 = 0$$

The deviation from the equilibrium can be defined as:  $\Delta x = x - x_e$  and we may also write,

$$\frac{d\Delta x}{dt} = \frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x^2$$

Subtraction of the second expression from the above yields

$$\frac{d\Delta x}{dt} = -k_1\Delta x - k_{-1}(\Delta x)^2 - 2k_{-1}x_e\Delta x$$

Since  $\Delta x$  is very small, the term in the  $(\Delta x)^2$  may be ignored. This will omission will produce,

$$\frac{d\Delta x}{dt} = -k_1\Delta x - 2k_{-1}x_e\Delta x$$

$$\frac{d\Delta x}{dt} = (-k_1 - 2k_{-1}x_e)\Delta x$$

Integrate this expression to obtain,

$$\int \frac{d\Delta x}{\Delta x} = \int (-k_1 - 2k_{-1}x_e) dt$$

$$\ln \Delta x = (-k_1 - 2k_{-1}x_e)t + I$$

Using the boundary condition  $t = 0$ ,  $\Delta x = \Delta x_0$ ,

$$\ln \frac{(\Delta x)_0}{\Delta x} = (-k_1 - 2k_{-1}x_e)t$$

By definition, the relaxation time  $t^*$  is the time that corresponds to,

$$\frac{(\Delta x)_0}{\Delta x} = e \text{ since } \ln(e) = 1 \text{ then,}$$

$$1 = (-k_1 - 2k_{-1}x_e)t^*$$

$$t^* = \frac{1}{(k_1 + 2k_{-1}x_e)}$$

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**9.25.** The rate constant for a reaction at 30 °C is found to be exactly twice the value at 20 °C. Calculate the activation energy.

**Solution:**

Given:  $k_{30\text{ °C}} = 2k_{20\text{ °C}}$

Required:  $E_a$

We are told that  $T_1 = 293.15\text{ K}$  and  $T_2 = 303.15\text{ K}$ . Let us take the inverse of these two temperatures in order to plot  $\ln(k)$  versus  $1/T$ . If this plot yields a straight line, then we know that the slope of this line is equal to the activation energy divided by  $R$ . We know that this is true according to the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln \frac{k_{20\text{ °C}}}{k_{30\text{ °C}}} = \frac{\cancel{\ln A} - \frac{E_a}{RT_1}}{\cancel{\ln A} - \frac{E_a}{RT_2}} \text{ therefore, } \ln k = \ln 2$$



$$\frac{1}{T_1} = \frac{1}{293.15 \text{ K}} = 3.411 \times 10^{-3} \text{ K}^{-1}$$

$$\frac{1}{T_2} = \frac{1}{303.15 \text{ K}} = 3.299 \times 10^{-3} \text{ K}^{-1}$$

$$m = \frac{\ln 2}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{0.693147}{(3.299 \times 10^{-3} - 3.411 \times 10^{-3}) \text{ K}^{-1}}$$

$$m = -6160 \text{ K} = \frac{E_a}{R}$$

$$E_a = -R \times m = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times -6160 \text{ K}$$

$$E_a = 51\,217.32 \text{ J mol}^{-1}$$

$$\boxed{E_a = 51.2 \text{ kJ mol}^{-1}}$$

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**9.26.** The rate constant for a reaction at 230 °C is found to be exactly twice the value at 220 °C. Calculate the activation energy.

**Solution:**

Given:  $k_{230\text{ }^{\circ}\text{C}} = 2k_{220\text{ }^{\circ}\text{C}}$

Required:  $E_a$

We are told that  $T_1 = 493.15\text{ K}$  and  $T_2 = 503.15\text{ K}$ . Let us take the inverse of these two temperatures in order to plot  $\ln(k)$  versus  $1/T$ . If this plot yields a straight line, then we know that the slope of this line is equal to the activation energy divided by  $R$ . We know that this is true according to the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln \frac{k_{220\text{ }^{\circ}\text{C}}}{k_{230\text{ }^{\circ}\text{C}}} = \frac{\cancel{\ln A} - \frac{E_a}{RT_1}}{\cancel{\ln A} - \frac{E_a}{RT_2}} \text{ therefore, } \ln k = \ln 2$$

$$\frac{1}{T_1} = \frac{1}{493.15 \text{ K}} = 2.028 \times 10^{-3} \text{ K}^{-1}$$

$$\frac{1}{T_2} = \frac{1}{503.15 \text{ K}} = 1.987 \times 10^{-3} \text{ K}^{-1}$$

$$m = \frac{\ln 2}{\frac{1}{T_2} - \frac{1}{T_1}} = \left| \frac{0.693147}{(1.987 \times 10^{-3} - 2.028 \times 10^{-3}) \text{ K}^{-1}} \right|$$

$$m = 17196 \text{ K} = \frac{E_a}{R}$$

$$E_a = 17196 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_a = 142976.142 \text{ J mol}^{-1}$$

$$\boxed{E_a = 143 \text{ kJ mol}^{-1}}$$

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**9.27.** The following data for a first-order decomposition reaction in aqueous medium was reported by E. O. Wiig [*J. Phys. Chem.* 34, 596(1930)].

$t/^{\circ}\text{C}$	0	20	40	60
$k/10^{-5} \text{ min}^{-1}$	2.46	43.5	575	5480

Find the activation energy and the preexponential factor.

**Solution:**

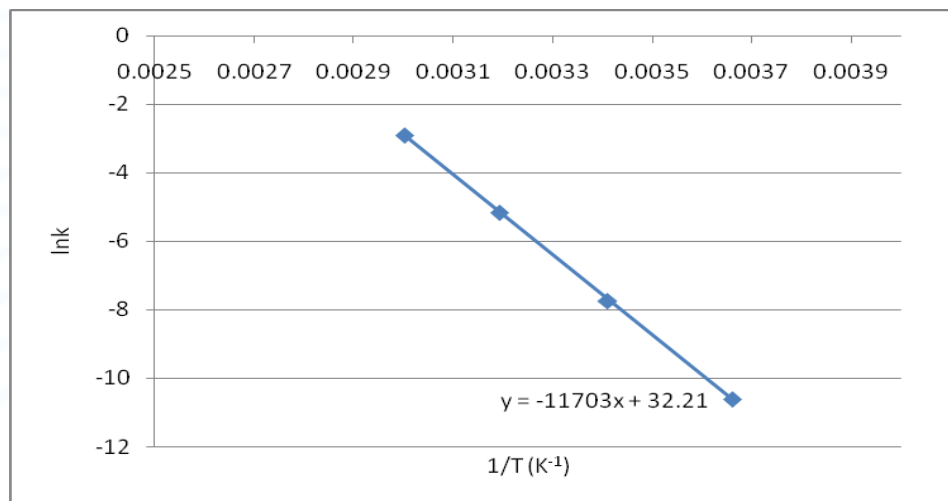
Given: see above

Required:  $E_a$ , A

Let us first change the temperature from Celsius to Kelvin, then proceed by taking the inverse value of each temperature and the  $\ln k$  for each value given above. We will then plot  $\ln k$  versus  $1/T$ . Since we have been told that this is a 1<sup>st</sup> order decomposition, this straight line will give us a slope which will enable us to determine the activation energy and in turn the pre-exponential factor.

T (K)	1/T ( $\text{K}^{-1}$ )	k ( $10^{-5} \text{ min}^{-1}$ )	$\ln k$
273.15	0.003661	2.46	-10.6128
293.15	0.003411	43.5	-7.74016
313.15	0.003193	575	-5.15856
333.15	0.003002	5480	-2.90407

It is either possible to perform a linear regression or simply add a trendline to the plot using Microsoft Excel in order to determine the equation of the line. Either method will produce the same results.



$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

When plotting  $\ln k$  versus  $1/T$ , you will find that  $\ln A$  is the  $y$ -intercept and that  $\frac{E_a}{R}$  is the slope.

$$\ln k = \ln A - \frac{E_a}{RT} = 32.217 - \frac{11703}{T}$$

$$E_a = 11703 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_a = 97304.59 \text{ J mol}^{-1}$$

$$E_a = 97.3 \text{ kJ mol}^{-1}$$

$$\ln A = 32.217$$

$$\cancel{\ln} e^A = e^{32.217}$$

$$A = 9.81 \times 10^{13} \text{ min}^{-1}$$

$$A = 1.63 \times 10^{12} \text{ s}^{-1}$$

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**9.28.** Two second-order reactions have identical preexponential factors and activation energies differing by  $20.0 \text{ kJ mol}^{-1}$ . Calculate the ratio of their rate constants (a) at  $0^\circ\text{C}$  and (b) at  $1000^\circ\text{C}$ .

**Solution:**

Given: two second order reactions:  $A_1 = A_2$ ,  $E_{a2} = E_{a1} + 20.00 \text{ kJ mol}^{-1}$

Required:  $\frac{k_1}{k_2}$  in each case

**a)** The ratio of their rate constants at  $0^\circ\text{C}$ .

$$k_1 = Ae^{-E_a/RT_1} \text{ and } k_2 = Ae^{-E_a/RT_2}$$

$$\text{ratio} = \frac{k_1}{k_2} = \frac{\cancel{A}e^{-E_a/RT}}{\cancel{A}e^{-E_a/RT}} \quad \text{this is true since both pre-exponential factors are identical.}$$

$$\frac{k_1}{k_2} = e^{\Delta E_a/RT} = e^{20\,000 \text{ J mol}^{-1} / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}$$

$$\boxed{\frac{k_1}{k_2}(273.15 \text{ K}) = 6.68 \times 10^3}$$

**b)** The ratio of their rate constants at  $1000^\circ\text{C}$

$$k_1 = Ae^{-E_a/RT_1} \text{ and } k_2 = Ae^{-E_a/RT_2}$$

$$\text{ratio} = \frac{k_1}{k_2} = \frac{\cancel{A}e^{-E_a/RT}}{\cancel{A}e^{-E_a/RT}} \quad \text{this is true since both pre-exponential factors are identical.}$$

$$\frac{k_1}{k_2} = e^{\Delta E_a/RT} = e^{20\,000 \text{ J mol}^{-1} / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(1273.15 \text{ K})}$$

$$\boxed{\frac{k_1}{k_2}(1273.15 \text{ K}) = 6.62}$$

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**9.29.** The gas-phase reaction between nitric oxide and oxygen is third order. The following rate constants have been measured:

$T/\text{K}$	80.0	143.0	228.0	300.0	413.0	564.0
$k \times 10^9/\text{cm}^6 \text{ mol}^{-1} \text{ s}^{-1}$	41.8	20.2	10.1	7.1	4.0	2.8

The behavior is interpreted in terms of a temperature-dependent preexponential factor; the rate equation is of the form:

$$k = aT^n e^{-E/RT}$$

where  $a$  and  $n$  are constants. Assume the activation energy to be zero and determine  $n$  to the nearest half-integer.

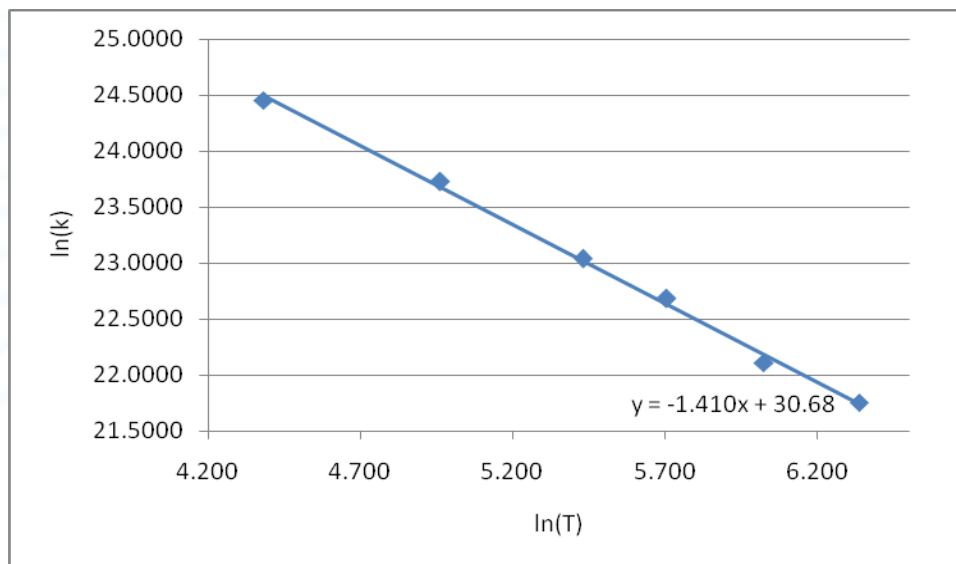
**Solution:**

Given: see above

Required:  $n$  to the nearest half-integer

We will begin by calculating the  $\ln(T)$  as well as the  $\ln(k)$  for each value given above.

$T \text{ (K)}$	$\ln(T)$	$k \text{ (cm}^6 \text{ mol}^{-1} \text{ s}^{-1}\text{)}$	$\ln(k)$
80	4.382	4.18E+10	24.4562
143	4.963	2.02E+10	23.7289
228	5.429	1.01E+10	23.0358
300	5.704	7.10E+09	22.6834
413	6.023	4.00E+09	22.1096
564	6.335	2.80E+09	21.7529



$$k = aT^n e^{-E/RT}$$

since  $a$  and  $n$  are constants and the activation energy is zero,

$$\ln k = \ln a + n \ln T - \frac{E}{RT}$$

$$\ln k = \ln a + n \ln T$$

This means that a plot of  $\ln(k)$  versus  $\ln(T)$  will create a line with a slope equal to  $n$  and the y-intercept is equal to  $\ln a$ .

$$\ln k = 30.68 - 1.410x$$

$$\boxed{n = -1.4}$$

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**9.30.** The definition of activation energy  $E_a$  is generally considered to be given by an extension of Eq. 9.91:

$$E_a = RT^2 \left( \frac{d \ln k}{dT} \right)$$

Problem 9.29 shows that for certain reactions, the temperature dependence of the reaction rate constant is better described by an expression of the type

$$k = aT^n e^{-E/RT}$$

Using the definition for  $E_a$  given here, derive an expression for the activation energy from this expression.

**Solution:**

Given that  $E_a = RT^2 \left( \frac{d \ln k}{dT} \right)$ , we can write;

$$k = aT^n e^{-E/RT}$$

$$\ln k = \ln a + n \ln T - \frac{E_a}{RT}$$

Take the derivative with respect to the temperature to obtain,

$$\frac{d \ln k}{dT} = \frac{d \ln a}{dT} + \frac{n d \ln T}{dT} - \frac{d \left( \frac{E}{RT} \right)}{dT}$$

$$\frac{d \ln k}{dT} = \frac{n}{T} + \frac{E}{RT^2}$$

$$E_a = RT^2 \left( \frac{d \ln k}{dT} \right) \text{ and } \frac{d \ln k}{dT} = \frac{n}{T} + \frac{E}{RT^2} \text{ then,}$$

$$E_a = RT^2 \left( \frac{n}{T} + \frac{E}{RT^2} \right)$$

$$E_a = \frac{nRT^2}{T} + \frac{E RT^2}{RT^2}$$

$$\boxed{E_a = nRT + E}$$

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**9.31.** The water flea *Daphnia* performs a constant number of heartbeats and then dies. The flea lives twice as long at 15 °C as at 25 °C. Calculate the activation energy for the reaction that controls the rate of its heartbeat.

**Solution:**

Given: *Daphnia*: lives twice as long at 15 °C as at 25 °C

Required:  $E_a$

We are told that  $T_1 = 288.15$  K and  $T_2 = 298.15$  K. Let us take the inverse of these two temperatures in order to plot  $\ln(k)$  versus  $1/T$ . If this plot yields a straight line, then we know that the slope of this line is equal to the activation energy divided by  $R$ . We know that this is true according to the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln \frac{k_{15^\circ\text{C}}}{k_{25^\circ\text{C}}} = \frac{\ln A - \frac{E_a}{RT_1}}{\ln A - \frac{E_a}{RT_2}}$$

$$\frac{1}{T_1} = \frac{1}{288.15 \text{ K}} = 3.470 \times 10^{-3} \text{ K}^{-1}$$

$$\frac{1}{T_2} = \frac{1}{298.15 \text{ K}} = 3.354 \times 10^{-3} \text{ K}^{-1}$$

$k_{25^\circ\text{C}} = 2k_{15^\circ\text{C}}$  therefore,

$$m = \frac{\ln 2}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{0.693147}{(3.354 \times 10^{-3} - 3.470 \times 10^{-3}) \text{ K}^{-1}}$$

$$m = 5974 \text{ K} = \frac{E_a}{R}$$

$$E_a = 5974 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_a = 49\,670.823 \text{ J mol}^{-1}$$

$$\boxed{E_a = 49.7 \text{ kJ mol}^{-1}}$$

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**9.32.** A sample of milk kept at 25 °C is found to sour 40 times as rapidly as when it is kept at 4 °C. Estimate the activation energy for the souring process.

**Solution:**

Given: milk: see above

Required:  $E_a$

We are told that  $T_1 = 277.15$  K and  $T_2 = 298.15$  K. Let us take the inverse of these two temperatures in order to plot  $\ln(k)$  versus  $1/T$ . If this plot yields a straight line, then we know that the slope of this line is equal to the activation energy divided by  $R$ . We know that this is true according to the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A \cancel{\ln e^{-E_a/RT}}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln \frac{k_{4^\circ\text{C}}}{k_{25^\circ\text{C}}} = \frac{\cancel{\ln A} - \frac{E_a}{RT_1}}{\cancel{\ln A} - \frac{E_a}{RT_2}} \text{ therefore, } \ln k = \ln 40$$

$$\frac{1}{T_1} = \frac{1}{277.15 \text{ K}} = 3.608 \times 10^{-3} \text{ K}^{-1}$$

$$\frac{1}{T_2} = \frac{1}{298.15 \text{ K}} = 3.354 \times 10^{-3} \text{ K}^{-1}$$

$$m = \frac{\ln 40}{\frac{1}{T_2} - \frac{1}{T_1}} = \left| \frac{0.693147}{(3.354 \times 10^{-3} - 3.608 \times 10^{-3}) \text{ K}^{-1}} \right|$$

$$m = 14\,500 \text{ K} = \frac{E_a}{R}$$

$$E_a = 14\,500 \cancel{\text{K}} \times 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1}$$

$$E_a = 120\,560.25 \text{ J mol}^{-1}$$

$$\boxed{E_a = 121 \text{ kJ mol}^{-1}}$$

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**\*9.33.** Experimentally, the rate constant for the  $\text{O}(^3\text{P}) + \text{HCl}$  reaction in the gas phase is found to have a temperature dependence given by:

$$k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 5.6 \times 10^{-21} T^{2.87} e^{-1766 \text{ K}/T}$$

in the range 350 – 1480 K [Mahmud, Kim, and Fontijn, *J. Phys. Chem.* 94, 2994(1990)].

**a.** Using the results of Problem 9.30, find the value of  $E_a$  at 900 K, which is approximately the middle of this range.

**b.** Using variational transition-state theory (an extension of the transition-state theory described in Section 9.9), the theoretical rate constant for this reaction is found to behave according to the equation:

$$k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 6.9 \times 10^{-20} T^{2.60} e^{-2454 \text{ K}/T}$$

in the same temperature range [T. C. Allison, B. Ramachandran, J. Senekowitsch, D. G. Truhlar, and R. E. Wyatt, *J. Mol. Structure, Theochem*, **454**, 307, 1998.] Compare the experimental and theoretical rate constants at 900 K.

**Solution:**

Given: see above, problem 9.30

Required:  $E_a$  (900 K), compare  $k_{\text{theoretical}}$  with  $k_{\text{experimental}}$

**a)** From the equation obtained by Mahmud, *et al.*,

$$E = 1766 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E = 14\,683.407 \text{ J mol}^{-1}$$

Using the expression derived in problem 9.30, we can determine the activation energy for this process at 900 K.

$$E_a = nRT + E$$

$$\text{since } k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 5.6 \times 10^{-21} T^{2.87} e^{-1766 \text{ K}/T} \text{ and } k = aT^n e^{-E/RT}$$

$$n = 2.87$$

$$E_a = (2.87) \left( 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) (900 \text{ K}) + 14\,683.407 \text{ J mol}^{-1}$$

$$E_a = 36\,159.7605 \text{ J mol}^{-1}$$

$$\boxed{E_a = 36.2 \text{ kJ mol}^{-1}}$$

b) Using variational transition-state theory in the same temperature range we find that,

$$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 5.6 \times 10^{-21} T^{2.87} e^{-1766 \text{ K}/T}$$

$$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 5.6 \times 10^{-21} (900^{2.87}) e^{-1766/900}$$

$$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 2.37 \times 10^{-13}$$

$$\boxed{k = 2.37 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}} \rightarrow \text{experimental}$$

$$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 6.9 \times 10^{-20} T^{2.60} e^{-2454 \text{ K}/T}$$

$$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 6.9 \times 10^{-20} (900^{2.60}) e^{-2454/900}$$

$$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 2.17 \times 10^{-13}$$

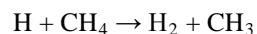
$$\boxed{k = 2.17 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}} \rightarrow \text{theoretical}$$

The theoretical value is slightly smaller than the experimental value. It is possible to perform a statistical analysis in order to determine the significance of this difference.

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**9.34.** The activation energy for the reaction:



has been measured to be  $49.8 \text{ kJ mol}^{-1}$ . Some estimates of enthalpies of formation,  $\Delta_f H^\circ$ , are:

$$\text{H} \quad 218.0 \text{ kJ mol}^{-1}$$

$$\text{CH}_4 \quad -74.8 \text{ kJ mol}^{-1}$$

$$\text{CH}_3 \quad 139.5 \text{ kJ mol}^{-1}$$

Estimate a value for the activation energy of the reverse reaction.

**Solution:**

Given: see above

Required:  $E_a$  (reverse reaction)

$$\begin{array}{ccccccc} & \text{H} & + & \text{CH}_4 & \rightarrow & \text{H}_2 & + & \text{CH}_3 \\ \Delta_f H^\circ (\text{kJ mol}^{-1}) & 218 & & -74.8 & & & & 139.5 \end{array}$$

Let us begin by determining the standard enthalpy for the reaction.

$$\Delta H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

$$\Delta H^\circ = \Delta_f H^\circ (\text{CH}_3) - [\Delta_f H^\circ (\text{CH}_4) + \Delta_f H^\circ (\text{H})]$$

$$\Delta H^\circ = [139.5 - (-74.8 + 218)] \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -3.7 \text{ kJ mol}^{-1}$$

From Figure 9.11, we can see that  $E_1 - E_{-1} = \Delta U$  (Eq. 9.70). In this particular instance it is possible to say that  $E_A - E_{-A} = \Delta H^\circ$ . Since we have been given the value for the activation energy for the forward reaction, we can use this expression to determine the activation energy for the reverse reaction.

Rearrange the above to obtain,

$$E_A - E_{-A} = \Delta H^\circ$$

$$E_{-A} = E_A - \Delta H^\circ$$

$$E_{-A} = [49.8 - (-3.7)] \text{ kJ mol}^{-1}$$

$$\boxed{E_{-A} = 53.5 \text{ kJ mol}^{-1}}$$

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**\*9.35.** By a treatment similar to that given for relaxation methods for the case  $A \rightleftharpoons Z$ , derive the rate equations for analyzing the reaction  $A + B \rightleftharpoons Z$  by carrying out the steps below.

**a.** Show that at equilibrium,  $k_1 a_e b_e = k_{-1} z_e$ , where the subscript  $e$  indicates equilibrium concentrations.

**b.** Show that  $\frac{dx}{dt} = k_1(a_e - x)(b_e - x) - k_{-1}(z_e + x)$ , where  $x$  represents a change from equilibrium.

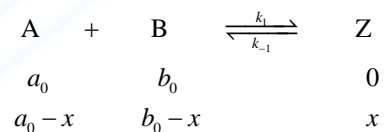
**c.** Show that for small  $x$ ,  $\frac{dx}{dt} = -[k_1(a_e + b_e) + k_{-1}]x$ . [Hint: Use the result of part (a).]

**d.** The displacement from equilibrium  $x$  always follows the first-order process  $x = x_0 \exp(-t/t^*)$ , where  $t^*$  is the relaxation time. Show that  $dx/dt = -x/t^*$ .

**e.** Comparing the results of parts (c) and (d), show that  $\frac{1}{t^*} = 2k_1 a_e + k_{-1}$  if  $a_e = b_e$ .

**f.** For the case  $a_e = b_e$ , show that  $\frac{1}{t^*} = 2\sqrt{k_1 k_{-1} z_e} + k_{-1}$ . [Hint: Use the result of part (e) and the fact that  $\frac{k_1}{k_{-1}} = \frac{z_e}{a_e b_e}$ .]

**Solution:**



**a)** First write out the rate law with respect to the rate of consumption of substances A and B.

$$\frac{dx}{dt} = k_1[A][B] - k_{-1}[Z] \text{ and at a time } t, \text{ we obtain:}$$

$$\frac{dx}{dt} = k_1(a_0 - x)(b_0 - x) - k_{-1}x \text{ however, at equilibrium,}$$

$$\frac{dx}{dt} = 0 \text{ and } x_e = \frac{a_0}{2}, \frac{b_0}{2}, z_e$$

$$\frac{dx}{dt} = k_1(a_0 - x)(b_0 - x) - k_{-1}x$$

$$k_1\left(a_0 - \frac{a_0}{2}\right)\left(b_0 - \frac{b_0}{2}\right) - k_{-1}z_e = 0$$

$$k_1 \frac{a_0}{2} \frac{b_0}{2} = k_{-1}z_e$$

Let  $\frac{a_0}{2} = a_e$  and  $\frac{b_0}{2} = b_e$  to simplify this expression further  $\rightarrow \boxed{k_1 a_e b_e = k_{-1} z_e}$

**b)** Since Z is formed as A and B are consumed, for a change in  $a_e$  and  $b_e$  by an amount  $-x$ , we obtain the following expression:

$$\boxed{\frac{d(z_e + x)}{dt} = \frac{dx}{dt} = k_1(a_e - x)(b_e - x) - k_{-1}(z_e + x)}$$

**c)** Show that for small  $x$ ,  $\frac{dx}{dt} = -[k_1(a_e + b_e) + k_{-1}]x$ .

We can multiply out the expression from part B to obtain,

$$\frac{dx}{dt} = k_1(a_e - x)(b_e - x) - k_{-1}(z_e + x)$$

$$\frac{dx}{dt} = k_1(a_e b_e - a_e x - b_e x + x^2) - k_{-1}(z_e + x)$$

$$\frac{dx}{dt} = k_1(a_e b_e - (a_e + b_e)x + x^2) - k_{-1}(z_e + x)$$

Since we are working under the assumption that  $x$  is small, we are able to drop a term from this equation.

$$\text{small } x \rightarrow \frac{dx}{dt} = k_1(a_e b_e - (a_e + b_e)x + x^2) - k_{-1}(z_e + x)$$

$$\frac{dx}{dt} = k_1(a_e b_e - (a_e + b_e)x) - k_{-1}(z_e + x)$$

Using the results from part A we find that,

$$\frac{dx}{dt} = k_1 a_e b_e - k_1(a_e + b_e)x - k_{-1}z_e - k_{-1}x$$

$$k_1 a_e b_e = k_{-1} z_e \text{ therefore,}$$

$$\frac{dx}{dt} = -k_1(a_e + b_e)x - \cancel{k_1 a_e b_e} - k_{-1}x + \cancel{k_1 a_e b_e}$$

$$\boxed{\frac{dx}{dt} = -[k_1(a_e + b_e) + k_{-1}]x}$$

d) Show that  $dx/dt = -x/t^*$ .

Since  $x = x_0 \exp\left(\frac{-t}{t^*}\right)$  we can differentiate both sides to obtain  $\frac{dx}{dt} = -\frac{x}{t^*}$ .

e) When comparing this result to that found in part C, we observe that,

$$-[k_1(a_e + b_e) + k_{-1}]x = -\frac{x}{t^*}$$

$$\frac{1}{t^*} = k_1(a_e + b_e) + k_{-1}$$

Let us assume for simplicity sake that  $b_e = a_e$ .

$$\boxed{\frac{1}{t^*} = 2k_1 a_e + k_{-1}}$$

f) Show that  $\frac{1}{t^*} = 2\sqrt{k_1 k_{-1} z_e} + k_{-1}$ .

For the equilibrium constant, we are told that  $\frac{k_1}{k_{-1}} = \frac{z_e}{a_e b_e}$ . We will use this fact in addition to the result obtained in part e) in order to prove the above statement.

$$K = \frac{k_1}{k_{-1}} = \frac{z_e}{a_e b_e} \text{ but when } b_e = a_e,$$

$$K = \frac{k_1}{k_{-1}} = \frac{z_e}{a_e^2}$$

$$\frac{a_e^2}{k_{-1}} = \frac{z_e}{k_1} \rightarrow a_e^2 = \frac{z_e k_{-1}}{k_1} \rightarrow a_e = \sqrt{\frac{z_e k_{-1}}{k_1}} \text{ and } k_1 = \frac{z_e k_{-1}}{a_e^2}$$

Substituting this into the expression generated in the previous section,

$$\frac{1}{t^*} = 2 \frac{\frac{z_e k_{-1}}{a_e^2}}{\frac{z_e k_{-1}}{k_1}} \sqrt{\frac{z_e k_{-1}}{k_1}} + k_{-1}$$

$$\frac{1}{t^*} = 2k_1 \sqrt{\frac{z_e k_{-1}}{k_1}} + k_{-1}$$

$$\boxed{\frac{1}{t^*} = 2\sqrt{k_1 k_{-1} z_e} + k_{-1}}$$

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**9.36.** A reaction of the type  $A + B \rightleftharpoons Z$  has been studied by relaxation methods. Some of the available data relating equilibrium concentrations of the product to the relaxation times are given below.

$z_e/M$	0.001	0.002	0.005	0.010	0.025	0.05	0.10
$t^*/ms$	4.08	3.74	2.63	1.84	1.31	0.88	0.674

Determine  $k_1$ ,  $k_{-1}$ , and  $K = k_1/k_{-1}$ .

**Solution:**

Given:  $z_e/M$  and  $t^*/ms$  given above

Required:  $k_1$ ,  $k_{-1}$ ,  $K = k_1/k_{-1}$

Recall from the previous problem,

$$K = \frac{k_1}{k_{-1}} = \frac{z_e}{a_e b_e} \text{ but when } b_e = a_e,$$

$$K = \frac{k_1}{k_{-1}} = \frac{z_e}{a_e^2}$$

$$\frac{a_e^2}{k_{-1}} = \frac{z_e k_{-1}}{k_1} \rightarrow a_e^2 = \frac{z_e k_{-1}}{k_1} \rightarrow a_e = \sqrt{\frac{z_e k_{-1}}{k_1}} \text{ and } k_1 = \frac{z_e k_{-1}}{a_e^2}$$

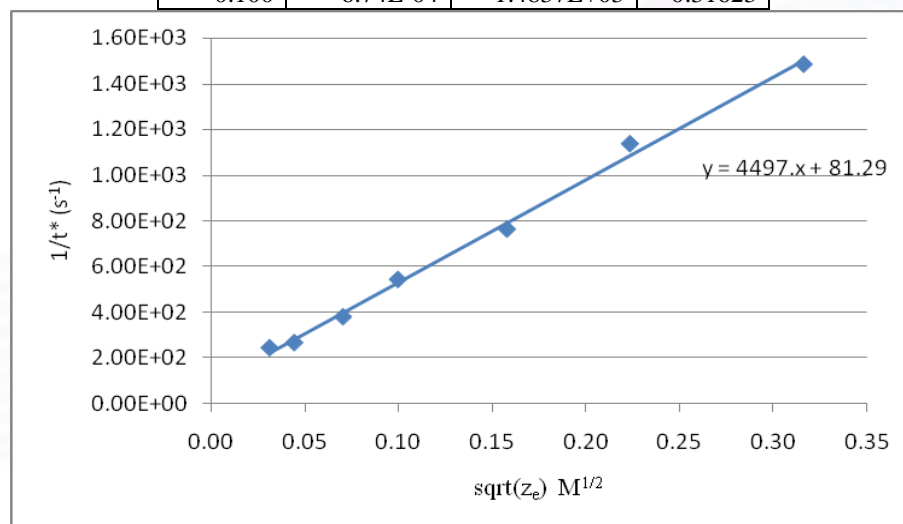
$$\frac{1}{t^*} = 2 \frac{z_e k_{-1}}{a_e^2} \sqrt{\frac{z_e k_{-1}}{k_1}} + k_{-1}$$

$$\frac{1}{t^*} = 2 \sqrt{k_1 k_{-1} z_e} + k_{-1}$$

|

From the above expression, we can see that the plot of  $\sqrt{z_e}$  vs.  $\frac{1}{t^*}$  will generate a straight line.

$z_e$	$t^*$ (s)	$1/t^*$ ( $s^{-1}$ )	$\text{sqrt}(z_e)$
0.001	4.08E-03	2.4510E+02	0.03162
0.002	3.74E-03	2.6738E+02	0.04472
0.005	2.63E-03	3.8023E+02	0.07071
0.010	1.84E-03	5.4348E+02	0.10000
0.025	1.31E-03	7.6336E+02	0.15811
0.050	8.80E-04	1.1364E+03	0.22361
0.100	6.74E-04	1.4837E+03	0.31623



It is possible to perform a linear regression on the data above in order to generate the equation for this line or one may use Microsoft Excel's trendline option which will display the equation of the line on the chart.

From the line equation, it can be observed that the y-intercept is equal to the rate constant for the reverse reaction ( $k_{-1}$ ).

$$k_{-1} = 81.3 \text{ s}^{-1}$$

Linear Regression Statistics			
<b>m</b>	4497.93	81.29022158	<b>b</b>
<b>Sm</b>	122.255	20.3000768	<b>Sb</b>
<b>R<sup>2</sup></b>	0.99632	31.27065583	<b>Sy</b>
<b>F</b>	1353.59	5	<b>DF</b>

From the linear regression statistics, we find that the rate constant for the forward reaction is equal to the regression error (third box from the top in the second column).

$$k_1 = 32.3 \text{ M}^{-1} \text{ s}^{-1}$$

Therefore,

$$K = \frac{k_1}{k_{-1}} = \frac{32.3 \text{ M}^{-1} \cancel{\text{s}^{-1}}}{81.3 \cancel{\text{s}^{-1}}}$$

$$K = 0.385 \text{ M}^{-1}$$

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**9.37.** The equilibrium  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  has a relaxation time of about  $40 \mu\text{s}$  at  $25^\circ\text{C}$ . Find the values of the forward and reverse rate constants.  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ .

(Hint: For this case, using steps similar to those of Problem 9.25, it can be shown that  $\frac{1}{t^*} = k_1 + k_{-1}([\text{H}^+]_e + [\text{OH}^-]_e)$ .)

**Solution:**

Given: see above

Required:  $k_1, k_{-1}$

Let us begin by writing down the rate of consumption of water for this reaction.

$$-\frac{d[\text{H}_2\text{O}]}{dt} = k_1[\text{H}_2\text{O}] - k_{-1}[\text{H}^+][\text{OH}^-]$$

From the equilibrium condition we may write,

$$k_1[\text{H}_2\text{O}]_e - k_{-1}[\text{H}^+]_e[\text{OH}^-]_e = 0$$

$$k_1[\text{H}_2\text{O}]_e = k_{-1}[\text{H}^+]_e[\text{OH}^-]_e$$

$$K = \frac{k_1}{k_{-1}} = \frac{[\text{H}^+]_e[\text{OH}^-]_e}{[\text{H}_2\text{O}]_e}$$

$$K_w = [\text{H}^+]_e[\text{OH}^-]_e = 10^{-14} \text{ therefore,}$$

$$K = \frac{K_w}{[\text{H}_2\text{O}]_e}$$

For 1 L of pure water,

$$C = \frac{n}{V}, n = \frac{m}{M} = \frac{1000 \cancel{\text{g}}}{18.0152 \cancel{\text{g}} \text{ mol}^{-1}} = 55.5087 \text{ mol}$$

$$[\text{H}_2\text{O}]_e = \frac{55.5087 \text{ mol}}{1 \text{ L}} = 55.51 \text{ M}$$

$$K = \frac{K_w}{[\text{H}_2\text{O}]_e} = \frac{10^{-14} \text{ M}^2}{55.51 \text{ M}} = 1.801\,52 \times 10^{-16} \text{ M}$$

Since  $k_1 = Kk_{-1}$ , then the equation that relates the relaxation time to the concentration can be written in the following manner:

$$\frac{1}{t^*} = Kk_{-1} + k_{-1}([\text{H}^+]_e + [\text{OH}^-]_e)$$

Factor to obtain,

$$\frac{1}{t^*} = k_{-1} [K + ([\text{H}^+]_e + [\text{OH}^-]_e)]$$

Using the fact that,  $\sqrt{K_w} = [\text{H}^+]_e = [\text{OH}^-]_e$  we can further simplify to get,

$$\frac{1}{t^*} = k_{-1} [K + 2\sqrt{K_w}]$$

This expression will enable us to solve for the rate constant belonging to the reverse reaction.

$$\frac{1}{t^*} = k_{-1} [K + 2\sqrt{K_w}]$$

$$k_{-1} = \frac{1}{t^* [K + 2\sqrt{K_w}]}$$

$$k_{-1} = \frac{1}{40 \times 10^{-6} \text{ s} [1.801\,52 \times 10^{-16} \text{ M} + 2\sqrt{10^{-14} \text{ M}^2}]}$$

$$\boxed{k_{-1} = 1.25 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}}$$

$$K = \frac{k_1}{k_{-1}}$$

$$k_1 = Kk_{-1} = (1.80152 \times 10^{-16} \text{ M}) (1.25 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1})$$

$$k_1 = 2.25 \times 10^{-5} \text{ s}^{-1}$$

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**9.38.** Two reactions of the same order have identical activation energies and their entropies of activation differ by  $50 \text{ J mol}^{-1}$ . Calculate the ratio of their rate constants at any temperature.

**Solution:**

Given:  $E_{a1} = E_{a2}$ ,  $S_{a2} = S_{a1} + 50 \text{ J K}^{-1} \text{ mol}^{-1}$

Required:  $\frac{k_1}{k_2}$  at any temperature

Using the Arrhenius equation,  $k = Ae^{-E_a/RT}$  we can formulate an expression which will enable us to determine the ratio of the rate constants at any temperature. For simplicity, we will allow the temperature to be  $273.15 \text{ K}$ .

$$k = e^2 \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta^\ddagger S^\circ}{R} \right) \exp \left( \frac{-E_a}{RT} \right)$$

$$k_1 = e^2 \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta^\ddagger S_1^\circ}{R} \right) \exp \left( \frac{-E_a}{RT} \right)$$

$$k_2 = e^2 \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta^\ddagger S_2^\circ}{R} \right) \exp \left( \frac{-E_a}{RT} \right)$$

$$\frac{k_1}{k_2} = \frac{e^2 \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta^\ddagger S_1^\circ}{R} \right) \exp \left( \frac{-E_a}{RT} \right)}{e^2 \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta^\ddagger S_2^\circ}{R} \right) \exp \left( \frac{-E_a}{RT} \right)}$$

$$\frac{k_1}{k_2} = \exp \left( \frac{\Delta^\ddagger S_1^\circ - \Delta^\ddagger S_2^\circ}{R} \right)$$

$$\frac{k_1}{k_2} = \exp \left( \frac{-50 \text{ J K}^{-1} \text{ mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right)$$

$$\boxed{\frac{k_1}{k_2} = 2.445 \times 10^{-3}}$$

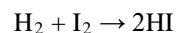
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**9.39.** The gas-phase reaction:



is second order. Its rate constant at 400 °C is  $2.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and its activation energy is  $150 \text{ kJ mol}^{-1}$ . Calculate  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$ , and  $\Delta^\ddagger G^\circ$  at 400 °C, and the preexponential factor.

**Solution:**

Given: second order:  $T = 400 \text{ }^\circ\text{C}$ ,  $k = 2.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $E_a = 150 \text{ kJ mol}^{-1}$

Required:  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$ ,  $\Delta^\ddagger G^\circ$ ,  $A$

It is easiest to determine the pre-exponential factor by using the given information in conjunction with the Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln A = \ln k + \frac{E_a}{RT}$$

$$\ln A = \ln(2.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) + \frac{150\,000 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(673.15 \text{ K})}$$

$$\ln A = 23.045\,504 \text{ [dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{]}$$

$$A = e^{23.045\,504 \text{ [dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{]}}$$

$$\boxed{A = 1.02 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

According to Eq. 9.100,

$$E_a = \Delta^\ddagger H^\circ + 2RT$$

Knowing the value for the activation energy, we can rearrange this expression in order to solve for  $\Delta^\ddagger H^\circ$ .

$$\Delta^\ddagger H^\circ = E_a - 2RT$$

$$\Delta^\ddagger H^\circ = 150\,000 \text{ J mol}^{-1} - (2 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 673.15 \text{ K})$$

$$\Delta^\ddagger H^\circ = 138\,806.1887 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger H^\circ = 138.8 \text{ kJ mol}^{-1}}$$

From Eq. 9.100, it follows that the rate constant may be written as,

$$k = e^2 \left( \frac{k_B T}{h} \right) e^{\Delta^\ddagger S^\circ / R} e^{-E_a / RT} \quad (\text{Eq. 9.101})$$

This can be rearranged in order to solve for  $\Delta^\ddagger S^\circ$ . This procedure yields,

$$k = e^2 \left( \frac{k_B T}{h} \right) e^{\Delta^\ddagger S^\circ / R} e^{-E_a / RT}$$

$$\frac{k}{e^{-E_a / RT}} = e^2 \left( \frac{k_B T}{h} \right) e^{\Delta^\ddagger S^\circ / R}$$

$$\frac{2.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{e^{\left( \frac{-150\,000 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} \right) (673.15 \text{ K})}} = e^2 \left( \frac{1.381 \times 10^{-23} \text{ J K}^{-1} (673.15 \text{ K})}{6.626 \times 10^{-34} \text{ J s}} \right) e^{\Delta^\ddagger S^\circ / R}$$

$$1.019\,847 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = (1.036\,676 \text{ s}^{-1}) e^{\Delta^\ddagger S^\circ / R}$$

$$e^{\Delta^\ddagger S^\circ / R} = \frac{1.019\,847 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{s}^{-1}}}{1.036\,676 \cancel{\text{s}^{-1}}}$$

$$\frac{\Delta^\ddagger S^\circ}{R} = \ln \left( \frac{1.019\,847 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{s}^{-1}}}{1.036\,676 \cancel{\text{s}^{-1}}} \right)$$

$$\frac{\Delta^\ddagger S^\circ}{R} = -9.226\,707$$

$$\Delta^\ddagger S^\circ = -9.226\,707 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{\Delta^\ddagger S^\circ = -76.72 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Recall from Chapter 3 that  $\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$  therefore,

$$\Delta^\ddagger G^\circ = 139\,000 \text{ J mol}^{-1} - (673.15 \text{ K}) (-76.72 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta^\ddagger G^\circ = 190\,641 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger G^\circ = 190.6 \text{ kJ mol}^{-1}}$$

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**9.40.** A substance decomposes according to first-order kinetics; the rate constants at various temperatures are as follows:

Temperature/ $^{\circ}\text{C}$	Rate constant, $k/\text{s}^{-1}$
15.0	$4.18 \times 10^{-6}$
20.0	$7.62 \times 10^{-6}$
25.0	$1.37 \times 10^{-5}$
30.0	$2.41 \times 10^{-5}$
37.0	$5.15 \times 10^{-5}$

Calculate the activation energy. Calculate also, at 25  $^{\circ}\text{C}$ , the enthalpy of activation, the Gibbs energy of activation, the preexponential factor, and the entropy of activation.

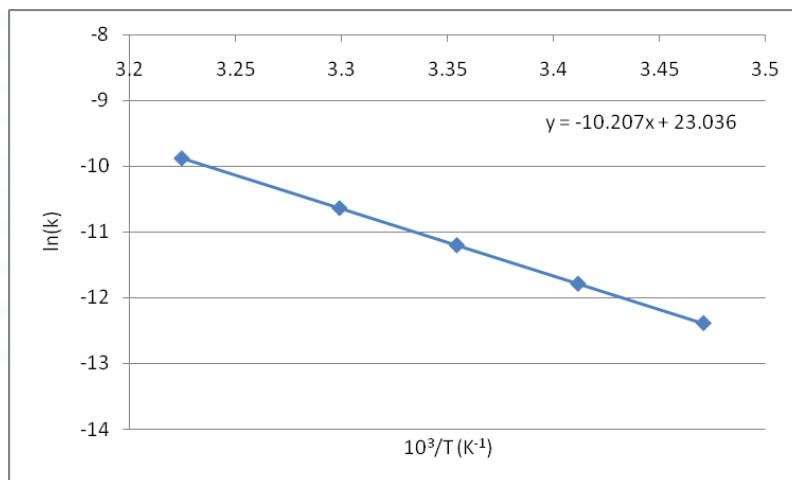
**Solution:**

Given: see above

Required:  $E_a$ ,  $\Delta^{\ddagger}H^{\circ}$ ,  $\Delta^{\ddagger}S^{\circ}$ ,  $\Delta^{\ddagger}G^{\circ}$ ,  $A$  at  $T = 25^{\circ}\text{C}$

Since we are dealing with a substance that decomposes according to 1<sup>st</sup> order kinetics, we may use the method of plotting  $\ln k$  versus  $1/T$  in order to generate a straight line curve.

T (K)	k ( $\text{s}^{-1}$ )	$10^3/T$ ( $\text{K}^{-1}$ )	$\ln(k)$
288.15	4.18E-06	3.470415	-12.3852
293.15	7.62E-06	3.411223	-11.7847
298.15	1.37E-05	3.354016	-11.1981
303.15	2.41E-05	3.298697	-10.6333
310.15	5.15E-05	3.224246	-9.87393



A linear regression may be performed in order to generate the equation for the line.

Linear Regression Statistics			
<b>m</b>	-10.2071	23.03635974	<b>b</b>
<b>Sm</b>	0.008403	0.028173779	<b>Sb</b>
<b>R<sup>2</sup></b>	0.999998	0.001609684	<b>Sy</b>
<b>F</b>	1475487	3	<b>DF</b>

The slope is therefore,  $m = -10.2071$ . Recall that from the Arrhenius equation, we are able to determine the activation energy once we know the slope.

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$m = \frac{E_a}{R}$$

$$E_a = |mR| = 10.2071 \times 10^3 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_a = 84\,866.933 \text{ J mol}^{-1}$$

$$\boxed{E_a = 84.9 \text{ kJ mol}^{-1}}$$

We will use the same methods employed in the previous problem to solve for the remaining variables.

$$E_a = \Delta^\ddagger H^\circ + RT \quad (\text{Eq. 9.95})$$

$$\Delta^\ddagger H^\circ = E_a - RT$$

$$\Delta^\ddagger H^\circ = 84\,867 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})$$

$$\Delta^\ddagger H^\circ = 82\,388.03 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger H^\circ = 82.4 \text{ kJ mol}^{-1}}$$

From Eq. 9.87 we know that,

$$k = \left(\frac{k_B T}{h}\right) \exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right)$$

Rearrange to obtain,

$$\frac{k}{\left(\frac{k_B T}{h}\right)} = \exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right)$$

$$\exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right) = \frac{1.37 \times 10^{-5} \cancel{\text{ s}^{-1}}}{\left(1.381 \times 10^{-23} \cancel{\text{ J K}^{-1}}\right)(298.15 \text{ K}) \cancel{6.626 \times 10^{-34} \cancel{\text{ J s}}}}$$

$$\exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right) = 2.204\,670 \times 10^{-18}$$

$$\frac{-\Delta^\ddagger G^\circ}{RT} = \ln(2.204\,670 \times 10^{-18})$$

$$\Delta^\ddagger G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)(298.15 \text{ K}) \ln(2.204\,670 \times 10^{-18})$$

$$\Delta^\ddagger G^\circ = 100\,785 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger G^\circ = 100.8 \text{ kJ mol}^{-1}}$$

$\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$  can be rearranged to obtain,

$$T\Delta^\ddagger S^\circ = \Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ$$

$$\Delta^\ddagger S^\circ = \frac{\Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ}{T} = \frac{82\,388 \text{ J mol}^{-1} - 100\,785 \text{ J mol}^{-1}}{298.15 \text{ K}}$$

$$\boxed{\Delta^\ddagger S^\circ = -61.7 \text{ J K}^{-1} \text{ mol}^{-1}}$$

For unimolecular gas reactions, the pre-exponential factor is given by Eq. 9.98.

$$A = e \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta^\ddagger S^\circ}{R} \right)$$

$$A = e \left( \frac{1.381 \times 10^{-23} (313.15)}{6.626 \times 10^{-34}} \right) \exp \left( \frac{-61.7}{8.3145} \right)$$

$$A = e (6.526\,715 \times 10^{12}) (5.97\,249 \times 10^{-4})$$

$$\boxed{A = 1.01 \times 10^{10} \text{ s}^{-1}}$$

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**9.41.** The following data have been obtained for the hydrolysis of adenosine triphosphate, catalyzed by hydrogen ions:

Temperature/°C	Rate constant, $k/s^{-1}$
39.9	$4.67 \times 10^{-6}$
43.8	$7.22 \times 10^{-6}$
47.1	$10.0 \times 10^{-6}$
50.2	$13.9 \times 10^{-6}$

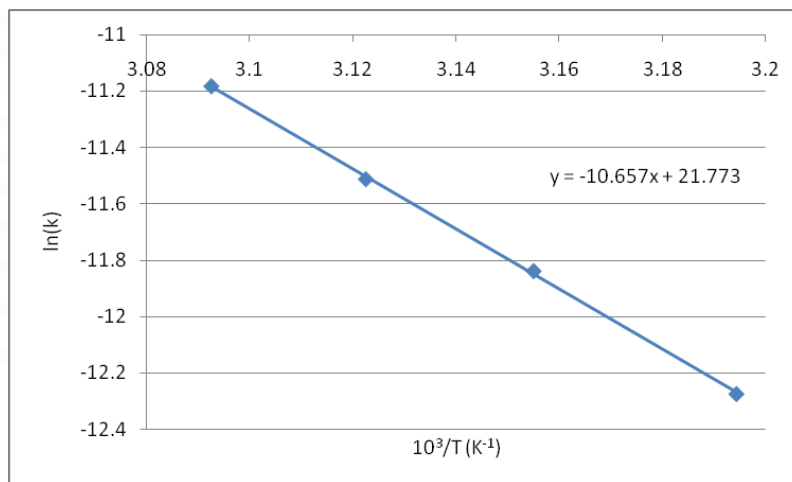
Calculate, at 40 °C, the Gibbs energy of activation, the energy of activation, the enthalpy of activation, the preexponential factor, and the entropy of activation.

**Solution:**

Given: see above

Required:  $E_a$ ,  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$ ,  $\Delta^\ddagger G^\circ$ ,  $A$  at  $T = 40$  °C

T (K)	k (s <sup>-1</sup> )	10 <sup>3</sup> /T (K <sup>-1</sup> )	ln(k)
313.05	4.67E-06	3.194378	12.2744
316.95	7.22E-06	3.155072	11.8387
320.25	1.00E-05	3.12256	11.5129
323.35	1.39E-05	3.092624	11.1836



Linear Regression Statistics			
<b>m</b>	-10.6571	21.77330432	<b>b</b>
<b>Sm</b>	0.14652	0.460276149	<b>Sb</b>
<b>R<sup>2</sup></b>	0.999622	0.011088537	<b>Sy</b>
<b>F</b>	5290.36	2	<b>DF</b>

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$m = \frac{E_a}{R}$$

$$E_a = |mR| = 10.6571 \times 10^3 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_a = 88\,608.45\,795 \text{ J mol}^{-1}$$

$$E_a = 88.6 \text{ kJ mol}^{-1}$$

$$E_a = \Delta^\ddagger H^\circ + RT$$

(Eq. 9.95)

$$\Delta^\ddagger H^\circ = E_a - RT$$

$$\Delta^\ddagger H^\circ = 88\,608 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 313.15 \text{ K})$$

$$\Delta^\ddagger H^\circ = 86\,003 \text{ J mol}^{-1}$$

$$\Delta^\ddagger H^\circ = 86.0 \text{ kJ mol}^{-1}$$

From Eq. 9.87 we know that,

$$k = \left(\frac{k_B T}{h}\right) \exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right)$$

Rearrange to obtain,

$$\frac{k}{\left(\frac{k_B T}{h}\right)} = \exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right)$$

We will estimate the rate constant at 40 °C by the rate constant given at 313.05 K.

$$\exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right) = \frac{4.67 \times 10^{-6} \cancel{\text{s}^{-1}}}{\frac{(1.381 \times 10^{-23} \cancel{\text{J K}^{-1}})(313.15 \cancel{\text{K}})}{6.626 \times 10^{-34} \cancel{\text{J s}}}}$$

$$\exp\left(\frac{-\Delta^\ddagger G^\circ}{RT}\right) = 7.155 \, 207 \times 10^{-19}$$

$$\frac{-\Delta^\ddagger G^\circ}{RT} = \ln(7.155 \, 207 \times 10^{-19})$$

$$\Delta^\ddagger G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)(313.15 \text{ K}) \ln(7.155 \, 207 \times 10^{-19})$$

$$\Delta^\ddagger G^\circ = 108 \, 785 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger G^\circ = 108.8 \text{ kJ mol}^{-1}}$$

$\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$  can be rearranged to obtain,

$$T\Delta^\ddagger S^\circ = \Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ$$

$$\Delta^\ddagger S^\circ = \frac{\Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ}{T} = \frac{86 \, 003 \text{ J mol}^{-1} - 108 \, 785 \text{ J mol}^{-1}}{313.15 \text{ K}}$$

$$\boxed{\Delta^\ddagger S^\circ = -72.751 \text{ J K}^{-1} \text{ mol}^{-1}}$$

For unimolecular gas reactions, the pre-exponential factor is given by Eq. 9.98.

$$A = e \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta^\ddagger S^\circ}{R} \right)$$

$$A = e \left( \frac{1.381 \times 10^{-23} (313.15)}{6.626 \times 10^{-34}} \right) \exp \left( \frac{-72.751}{8.3145} \right)$$

$$A = e (6.526\,715 \times 10^{12}) (1.584\,780\,021 \times 10^{-4})$$

$$\boxed{A = 2.81 \times 10^9 \text{ s}^{-1}}$$

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**9.42.** The half-life of the thermal denaturation of hemoglobin, a first-order process, has been found to be 3460 s at 60 °C and 530 s at 65 °C. Calculate the enthalpy of activation and entropy of activation at 60 °C, assuming the Arrhenius equation to apply.

**Solution:**

Given: first order:  $t_{1/2}(60\text{ °C}) = 3460\text{ s}$ ,  $t_{1/2}(65\text{ °C}) = 530\text{ s}$

Required:  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$  at  $T = 60\text{ °C}$

Since this is a 1<sup>st</sup> order process, we know that  $t_{1/2} = \frac{\ln 2}{k}$ . Let us determine the values of the rate constant at 60 °C and 65 °C.

$$k(60\text{ °C}) = \frac{\ln 2}{t_{1/2}(60\text{ °C})} = \frac{0.693\,147}{3460\text{ s}}$$

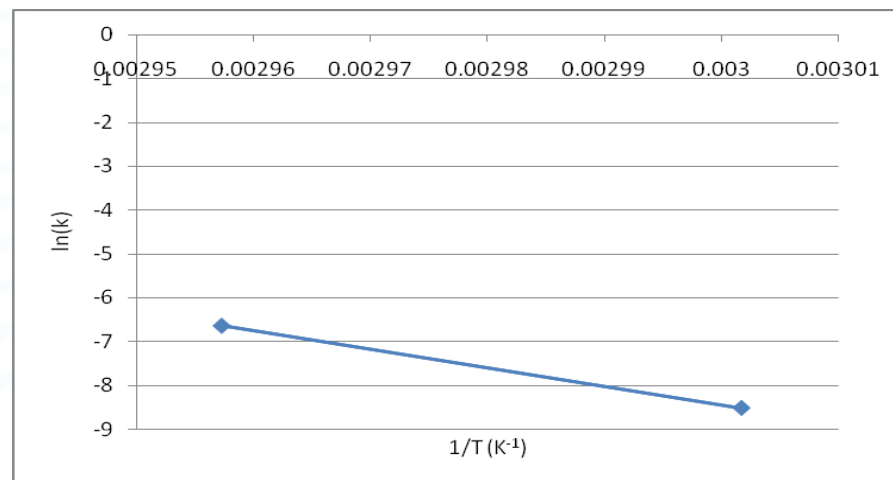
$$k(60\text{ °C}) = 2.003\,316 \times 10^{-4}\text{ s}^{-1}$$

$$k(65\text{ °C}) = \frac{\ln 2}{t_{1/2}(65\text{ °C})} = \frac{0.693\,147}{530\text{ s}}$$

$$k(65\text{ °C}) = 1.307\,825 \times 10^{-3}\text{ s}^{-1}$$

Taking the inverse of both temperatures will enable us to generate a straight line plot. As previously seen, the slope of this curve allows us to calculate the activation energy.

T (K)	1/T (K <sup>-1</sup> )	k <sub>1</sub> (s <sup>-1</sup> )	k <sub>2</sub> (s <sup>-1</sup> )	ln(k <sub>1</sub> )	ln(k <sub>2</sub> )	ln(k <sub>2</sub> /k <sub>1</sub> )
333.15	0.003002	2.00E-04	1.31E-03	-8.51554	-6.63939	1.876147
338.15	0.002957					



$$m = \frac{\text{rise}}{\text{run}} = \frac{\ln k_2 - \ln k_1}{1/T_2 - 1/T_1} = \frac{1.876\,147}{(2.957 \times 10^{-3} - 3.002 \times 10^{-3}) \text{ K}^{-1}}$$

$$m = -42\,271 \text{ K} = -\frac{E_a}{R}$$

$$E_a = (-42\,271 \text{ K}) \left( -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right)$$

$$E_a = 351\,444 \text{ J mol}^{-1}$$

$$\boxed{E_a = 351.4 \text{ kJ mol}^{-1}}$$

$$E_a = \Delta^\ddagger H^\circ + RT$$

(Eq. 9.95)

$$\Delta^\ddagger H^\circ = E_a - RT$$

$$\Delta^\ddagger H^\circ = 351\,444 \text{ J mol}^{-1} - \left( 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 333.15 \text{ K} \right)$$

$$\Delta^\ddagger H^\circ = 348\,674 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger H^\circ = 348.7 \text{ kJ mol}^{-1}}$$

$$k = \left( \frac{k_B T}{h} \right) \exp \left( \frac{-\Delta^\ddagger G^\circ}{RT} \right) \rightarrow \frac{k}{\left( \frac{k_B T}{h} \right)} = \exp \left( \frac{-\Delta^\ddagger G^\circ}{RT} \right)$$

$$\exp \left( \frac{-\Delta^\ddagger G^\circ}{RT} \right) = \frac{2.003 \, 316 \times 10^{-4} \, \cancel{\text{ s}^{-1}}}{\frac{(1.381 \times 10^{-23} \, \cancel{\text{ J K}^{-1}})(333.15 \, \text{ K})}{6.626 \times 10^{-34} \, \cancel{\text{ J s}}}}$$

$$\exp \left( \frac{-\Delta^\ddagger G^\circ}{RT} \right) = 2.885 \, 143 \times 10^{-17}$$

$$\frac{-\Delta^\ddagger G^\circ}{RT} = \ln(2.885 \, 143 \times 10^{-17})$$

$$\Delta^\ddagger G^\circ = -\left(8.3145 \, \text{ J K}^{-1} \text{ mol}^{-1}\right)(333.15 \, \text{ K}) \ln(2.885 \, 143 \times 10^{-17})$$

$$\Delta^\ddagger G^\circ = 105 \, 493 \, \text{ J mol}^{-1}$$

$\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$  can be rearranged to obtain,

$$T\Delta^\ddagger S^\circ = \Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ$$

$$\Delta^\ddagger S^\circ = \frac{\Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ}{T} = \frac{348 \, 674 \, \text{ J mol}^{-1} - 105 \, 493 \, \text{ J mol}^{-1}}{333.15 \, \text{ K}}$$

$$\boxed{\Delta^\ddagger S^\circ = 729.95 \, \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**\*9.43. a.** Using Eq. 9.73, calculate the collision density for  $6.022 \times 10^{23}$  molecules of hydrogen iodide present in a volume  $1 \text{ m}^3$  at  $300 \text{ K}$ . Take  $d_{\text{AA}} = 0.35 \text{ nm}$ .

**b.** If the activation energy for the decomposition of HI is  $184 \text{ kJ mol}^{-1}$ , what rate constant does kinetic theory predict at  $300 \text{ }^\circ\text{C}$ ? To what entropy of activation does this result correspond?

**Solution:**

Given: Eq. 73,  $6.022 \times 10^{23}$  molecules of HI,  $V = 1 \text{ m}^3$ ,  $T = 300 \text{ K}$ ,  $d_{\text{AA}} = 0.35 \text{ nm}$

$$E_a = 184 \text{ kJ mol}^{-1}, T = 300 \text{ }^\circ\text{C}$$

Required:  $Z_{\text{AA}}$ ,  $\Delta^\ddagger S^\circ$

Eq. 9.73 defines the collision density,

$$Z_{\text{AA}} = 2d^2 N_A^2 \sqrt{\frac{\pi k_B T}{m}}$$

**a)** First we need to find the mass of hydrogen iodide.

$$m = \frac{M}{N_A} = \frac{127.904 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$m = 2.123\,946 \times 10^{-22} \text{ g}$$

$$m = 2.123\,946 \times 10^{-25} \text{ kg}$$

Now we can simply substitute all appropriate values into Eq. 9.73 to obtain the collision density.

$$Z_{\text{AA}} = 2(0.35 \times 10^{-9} \text{ m})^2 (6.022 \times 10^{23} \text{ m}^{-3})^2 \sqrt{\frac{\pi(1.381 \times 10^{-23} \text{ J K}^{-1})(573.15 \text{ K})}{2.123\,946 \times 10^{-25} \text{ kg}}}$$

$$\boxed{Z_{\text{AA}} = 3.040 \times 10^{31} \text{ m}^{-3} \text{ s}^{-1}}$$

**b)** We can now use a version of Eq. 9.78 in order to determine the value of the rate constant.

$$\nu = Z_{AA} e^{-E_a/RT}$$

$$\nu = (3.040 \times 10^{31} \text{ m}^{-3} \text{ s}^{-1}) e^{-184\,000/(8.3145 \times 573.15)}$$

$$\nu = 5.179 \times 10^{14} \text{ m}^{-3} \text{ s}^{-1}$$

$$n = \frac{m}{M} = \frac{2.123\,946 \times 10^{-22} \text{ g}}{127.904 \text{ g mol}^{-1}}$$

$$n = 1.660\,578 \text{ mol}$$

$$\nu = 5.179 \times 10^{14} \text{ m}^{-3} \text{ s}^{-1} \times 1.660\,578 \text{ mol}$$

$$\nu = 8.600\,135 \times 10^{-10} \text{ mol m}^{-3} \text{ s}^{-1}$$

According to the rate equation,

$$\nu = k [\text{HI}]^2$$

$$k = \frac{\nu}{[\text{HI}]^2} = \frac{8.600\,135 \times 10^{-10} \text{ mol m}^{-3} \text{ s}^{-1}}{(1 \text{ mol m}^{-3})^2}$$

$$k = 8.600\,135 \times 10^{-10} \text{ mol}^{-1} \text{ s}^{-1} \times \frac{1000 \text{ dm}^3}{1 \text{ m}^3}$$

$$k = 8.600\,135 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The collision frequency factor (ie. pre-exponential factor) is given by,

$$A = \frac{k}{e^{-E_a/RT}} = \frac{8.600\,135 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{e^{-184\,000/(8.3145 \times 573.15)}}$$

$$A = 5.048\,238 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

In order to obtain the value for the entropy of activation we may use Eq. 9.98 but for a bimolecular molecule.

$$A = e^2 \left( \frac{k_B T}{h} \right) e^{\dagger \Delta S/R}$$

Rearranging,

$$e^{\ddagger\Delta S/R} = \frac{5.048\,238 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{ s}^{-1}}}{e^2 \left( \frac{(1.381 \times 10^{-23} \cancel{\text{ J}} \cancel{\text{ K}^{-1}}) 573.15 \cancel{\text{ K}}}{6.626 \times 10^{-34} \cancel{\text{ J}} \cancel{\text{ s}}} \right)}$$

$$e^{\ddagger\Delta S/R} = 5.719\,266 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1}$$

$$\Delta^\ddagger S^\circ = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(5.719\,266 \times 10^{-4})$$

$$\boxed{\Delta^\ddagger S^\circ = -62.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**9.44.** The rate constant for a first-order reaction is  $7.40 \times 10^{-9} \text{ s}^{-1}$  at  $25^\circ\text{C}$ , and the activation energy is  $112.0 \text{ kJ mol}^{-1}$ . Calculate, at  $25^\circ\text{C}$ , the preexponential factor  $A$ , the enthalpy of activation  $\Delta^\ddagger H^\circ$ , the Gibbs energy of activation  $\Delta^\ddagger G^\circ$ , and the entropy of activation  $\Delta^\ddagger S^\circ$ .

**Solution:**

Given: first order:  $k = 7.40 \times 10^{-9} \text{ s}^{-1}$ ,  $T = 25^\circ\text{C}$ ,  $E_a = 112.0 \text{ kJ mol}^{-1}$

Required:  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$ ,  $\Delta^\ddagger G^\circ$ ,  $A$  at  $T = 25^\circ\text{C}$

Given the rate constant, we may first solve for the Gibbs energy of activation using Eq. 9.87.

$$k = \left( \frac{k_B T}{h} \right) e^{-\Delta^\ddagger G^\circ / RT}$$

$$e^{-\Delta^\ddagger G^\circ / RT} = \frac{7.40 \times 10^{-9} \cancel{\text{ s}^{-1}}}{\left( 1.381 \times 10^{-23} \cancel{\text{ J K}^{-1}} \right) (298.15 \text{ K})} \frac{1}{6.626 \times 10^{-34} \cancel{\text{ J s}}}$$

$$e^{-\Delta^\ddagger G^\circ / RT} = 1.190\,843 \times 10^{-21}$$

$$\frac{-\Delta^\ddagger G^\circ}{RT} = \ln(1.190\,843 \times 10^{-21})$$

$$\Delta^\ddagger G^\circ = -\left( 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) (298.15 \text{ K}) \ln(1.190\,843 \times 10^{-21})$$

$$\Delta^\ddagger G^\circ = 119\,436 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger G^\circ = 119.4 \text{ kJ mol}^{-1}}$$

Given the activation energy, we may first solve for the enthalpy of activation using Eq. 9.95.

$$E_a = \Delta^\ddagger H^\circ + RT \quad (\text{Eq. 9.95})$$

$$\Delta^\ddagger H^\circ = E_a - RT$$

$$\Delta^\ddagger H^\circ = 112\,000 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})$$

$$\Delta^\ddagger H^\circ = 109\,521 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger H^\circ = 109.5 \text{ kJ mol}^{-1}}$$

$\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$  can be rearranged to obtain,

$$T\Delta^\ddagger S^\circ = \Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ$$

$$\Delta^\ddagger S^\circ = \frac{\Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ}{T} = \frac{109\,521 \text{ J mol}^{-1} - 119\,436 \text{ J mol}^{-1}}{298.15 \text{ K}}$$

$$\boxed{\Delta^\ddagger S^\circ = -33.25 \text{ J K}^{-1} \text{ mol}^{-1}}$$

For unimolecular gas reactions, the pre-exponential factor is given by Eq. 9.98.

$$A = e \left( \frac{k_B T}{h} \right) e^{\Delta^\ddagger S^\circ / R}$$

$$A = e \left( \frac{1.381 \times 10^{-23} (298.15)}{6.626 \times 10^{-34}} \right) e^{(-33.254\,966)/(8.3145)}$$

$$A = e (6.214\,083 \times 10^{12}) (0.018\,322)$$

$$\boxed{A = 3.09 \times 10^{11} \text{ s}^{-1}}$$

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**9.45.** The rate constant for a second-order reaction in solution is  $3.95 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ , and the activation energy is  $120.0 \text{ kJ mol}^{-1}$ . Calculate, at  $25^\circ\text{C}$ , the preexponential factor  $A$ , the enthalpy of activation  $\Delta^\ddagger H^\circ$ , the Gibbs energy of activation  $\Delta^\ddagger G^\circ$ , and the entropy of activation  $\Delta^\ddagger S^\circ$ .

**Solution:**

Given: first order:  $k = 3.95 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $T = 25^\circ\text{C}$ ,  $E_a = 120.0 \text{ kJ mol}^{-1}$

Required:  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$ ,  $\Delta^\ddagger G^\circ$ ,  $A$  at  $T = 25^\circ\text{C}$

Given the rate constant, we may first solve for the Gibbs energy of activation using Eq. 9.87.

$$k = \left( \frac{k_B T}{h} \right) e^{-\Delta^\ddagger G^\circ / RT}$$

$$e^{-\Delta^\ddagger G^\circ / RT} = \frac{3.95 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{s}^{-1}}}{\frac{(1.381 \times 10^{-23} \cancel{\text{J K}^{-1}})(298.15 \text{ K})}{6.626 \times 10^{-34} \cancel{\text{J s}}}}$$

$$e^{-\Delta^\ddagger G^\circ / RT} = 6.356\,529 \times 10^{-17}$$

$$\frac{-\Delta^\ddagger G^\circ}{RT} = \ln(6.356\,529 \times 10^{-17})$$

$$\Delta^\ddagger G^\circ = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)(298.15 \text{ K}) \ln(6.356\,529 \times 10^{-17})$$

$$\Delta^\ddagger G^\circ = 92\,452 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger G^\circ = 92.45 \text{ kJ mol}^{-1}}$$

Given the activation energy, we may first solve for the enthalpy of activation using Eq. 9.95.

$$E_a = \Delta^\ddagger H^\circ + RT \quad (\text{Eq. 9.95})$$

$$\Delta^\ddagger H^\circ = E_a - RT$$

$$\Delta^\ddagger H^\circ = 120\,000 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})$$

$$\Delta^\ddagger H^\circ = 117\,521 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger H^\circ = 117.5 \text{ kJ mol}^{-1}}$$

$\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$  can be rearranged to obtain,

$$T\Delta^\ddagger S^\circ = \Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ$$

$$\Delta^\ddagger S^\circ = \frac{\Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ}{T} = \frac{117\,521 \text{ J mol}^{-1} - 92\,452 \text{ J mol}^{-1}}{298.15 \text{ K}}$$

$$\boxed{\Delta^\ddagger S^\circ = 84.08 \text{ J K}^{-1} \text{ mol}^{-1}}$$

For unimolecular gas reactions, the pre-exponential factor is given by Eq. 9.98.

$$A = e \left( \frac{k_B T}{h} \right) e^{\Delta^\ddagger S^\circ / R}$$

$$A = e \left( \frac{1.381 \times 10^{-23} (298.15)}{6.626 \times 10^{-34}} \right) e^{(84.08)/(8.3145)}$$

$$A = e (6.214\,083 \times 10^{12}) (24\,654)$$

$$\boxed{A = 4.16 \times 10^{17} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

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**9.46.** The rate constant  $k$  for the reaction between persulfate ions and iodide ions varies with ionic strength  $I$  as follows:

$I/10^{-3} \text{ mol dm}^{-3}$	2.45	3.65	4.45	6.45	8.45	12.4
$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.05	1.12	1.16	1.18	1.26	1.39

Estimate the value of  $z_A z_B$ .

**Solution:**

We know that this reaction follows 2<sup>nd</sup> order kinetics by examining the units associated with the rate constant. Recall that information regarding the rate law, rate constant and half life are condensed in Table 9.1.

According to the Debye-Huckel limiting law (Section 7.10) the activity coefficient of an ion is related to its valency,  $z$  and the ionic strength,  $I$ . By Eq. 7.104,

$$\log_{10} \gamma = -Bz^2 \sqrt{I} \quad (\text{Eq. 9.121})$$

Introduction of the above into the rate equation (Eq. 9.120) gives,

$$\log_{10} k = \log_{10} k_0 + \log_{10} \frac{\gamma_A \gamma_B}{\gamma^\ddagger} \quad (\text{Eq. 9.120})$$

$$\log_{10} k = \log_{10} k_0 + \log_{10} \gamma_A + \log_{10} \gamma_B - \log_{10} \gamma^\ddagger$$

$$\log_{10} k = \log_{10} k_0 - B \left[ z_A^2 + z_B^2 - (z_A + z_B)^2 \right] \sqrt{I}$$

$$\log_{10} k = \log_{10} k_0 - B \left[ \cancel{z_A^2} + \cancel{z_B^2} - \left( \cancel{z_A^2} + 2z_A z_B + \cancel{z_B^2} \right) \right] \sqrt{I}$$

$$\log_{10} k = \log_{10} k_0 + 2Bz_A z_B \sqrt{I}$$

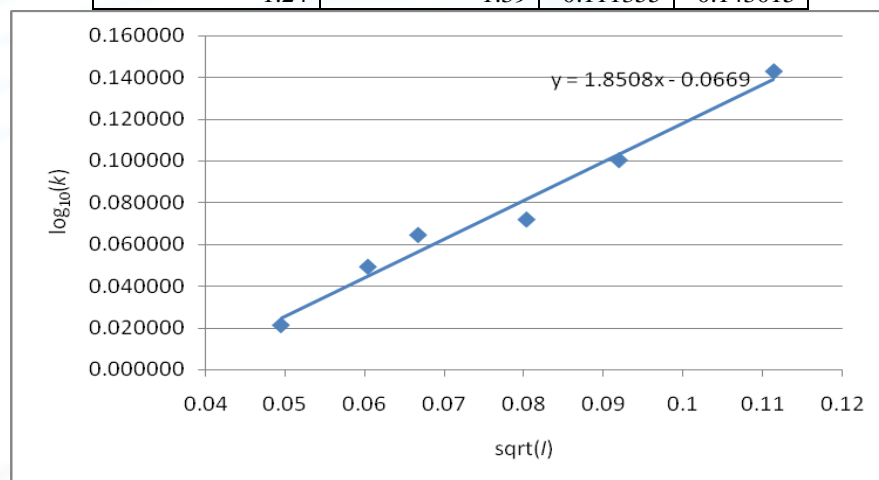
The value of  $B$  is approximately  $0.51 \text{ dm}^{-3/2} \text{ mol}^{-1/2}$  for aqueous solutions at 25 °C. Therefore,

$$\log_{10} k = \log_{10} k_0 + 1.02 z_A z_B \sqrt{I / \text{mol dm}^{-3}} \quad (\text{Eq. 9.125})$$

$I (10^{-3} \text{ mol dm}^{-3})$	$k (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$\text{sqrt}(I)$	$\log_{10}(k)$
-----------------------------------	---	------------------	----------------



2.45	1.05	0.049497	0.021189
3.65	1.12	0.060415	0.049218
4.45	1.16	0.066708	0.064458
6.45	1.18	0.080312	0.071882
8.45	1.26	0.091924	0.100371
1.24	1.39	0.111355	0.143015



Linear Regression Statistics			
<b>m</b>	1.850795931	-0.066937665	<b>b</b>
<b>Sm</b>	0.144547247	0.011480668	<b>Sb</b>
<b>R<sup>2</sup></b>	0.976182639	0.007300432	<b>Sy</b>
<b>F</b>	163.9447163	4	<b>DF</b>

$$\log_{10} k - \log_{10} k_0 \approx z_A z_B \sqrt{I / \text{mol dm}^{-3}}$$

Therefore, a plot of  $\log_{10} k$  against  $\sqrt{I / \text{mol dm}^{-3}}$  will yield a slope that is approximately equal to  $z_A z_B$ . From the regression statistics, we see that  $m = 1.850\,796$

$$z_A z_B = \frac{1.850\,795\,931}{1.02} = 1.814\,505\,814$$

$$\boxed{z_A z_B \approx 1.814}$$

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**9.47.** The following constants were obtained by Brønsted and Livingstone [*J. Amer. Chem. Soc.*, 49, 435(1927)] for the reaction:  

$$[\text{CoBr}(\text{NH}_3)_5]^{2+} + \text{OH}^- \rightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{2+} + \text{Br}^-$$
  
 under the following conditions:

$[\text{CoBr}(\text{NH}_3)_5]^{2+}$	Concentration/mol dm <sup>-1</sup>		$k$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
	NaOH	NaCl	
$5.0 \times 10^{-4}$	$7.95 \times 10^{-4}$	0	1.52
$5.96 \times 10^{-4}$	$1.004 \times 10^{-3}$	0	1.45
$6.00 \times 10^{-4}$	$0.696 \times 10^{-3}$	0.005	1.23
$6.00 \times 10^{-4}$	$0.696 \times 10^{-3}$	0.020	0.97
$6.00 \times 10^{-4}$	$0.691 \times 10^{-3}$	0.030	0.91

Make an estimate of the rate constant of the reaction at zero ionic strength. Are the results consistent with  $z_A z_B = -2$ ?

**Solution:**

Let us begin by determining the ionic strengths of each reaction mixture. Recall that the ionic strength of a solution represents a function of all ions present into the given solution.

$$I = \frac{1}{2} \sum_{B=1}^n c_B z_B^2$$

where  $c_B$  = molar concentration of each ion and  $z_B$  = charge number of that particular ion.

$$(1) \quad I = \frac{1}{2} \left[ (2^2 \times 5.0 \times 10^{-4}) + (1.0 \times 10^{-3}) + (2 \times 7.95 \times 10^{-4}) \right]$$

$$I = 2.295 \times 10^{-3} \text{ M}$$

$$(2) \quad I = \frac{1}{2} \left[ (2^2 \times 5.96 \times 10^{-4}) + (11.92 \times 10^{-4}) + (2 \times 1.004 \times 10^{-3}) \right]$$

$$I = 2.79 \times 10^{-3} \text{ M}$$

$$(3) \quad I = \frac{1}{2} \left[ (2^2 \times 6.0 \times 10^{-4}) + (12.0 \times 10^{-4}) + (2 \times 0.696 \times 10^{-3}) + 0.01 \right]$$

$$I = 7.496 \times 10^{-3} \text{ M}$$

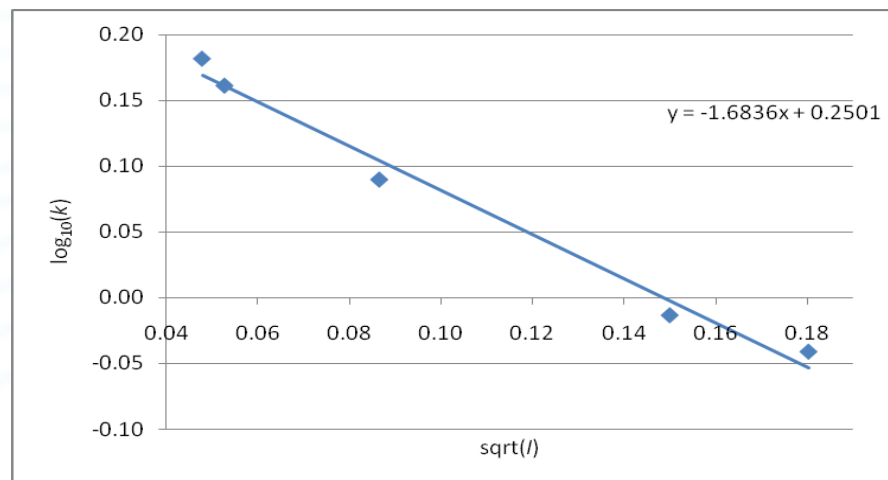
$$(4) \quad I = \frac{1}{2} \left[ (24.0 \times 10^{-4}) + (12.0 \times 10^{-4}) + (1.392 \times 10^{-3}) + 0.04 \right]$$

$$I = 22.50 \times 10^{-3} \text{ M}$$

$$(5) \quad I = \frac{1}{2} \left[ (24.0 \times 10^{-4}) + (12.0 \times 10^{-4}) + (1.392 \times 10^{-3}) + 0.06 \right]$$

$$I = 32.50 \times 10^{-3} \text{ M}$$

$I (10^{-3} \text{ mol dm}^{-3})$	$k (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$\text{sqrt}(I)$	$\log_{10}(k)$
2.30E-03	1.52	0.047906	0.181844
2.79E-03	1.45	0.052820	0.161368
7.50E-03	1.23	0.086579	0.089905
2.25E-02	0.97	0.150000	-0.013228
3.25E-02	0.91	0.180278	-0.040959



linear regression statistics:	
-1.683623642	0.250069168
0.122806104	0.014277339
0.984289358	0.01453188
187.9533719	3

From the regression statistics, we can see that the y-intercept is equal to  $\log_{10} k_0 = 0.250\,0691\,68$ .

We may now make an estimate of the rate constant.

$$k_0 = 10^{0.250\,0691\,68}$$

$$k_0 = 1.778\,562\,651$$

$$k_0 = 1.78 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Again from the regression statistics, the slope was given to be  $m = -1.683\,623\,642$ . We already know that the slope is equal to  $1.02z_A z_B$  for an aqueous solution at 25 °C. Therefore,

$$m = -1.683\,623\,642 = 1.02z_A z_B$$

$$z_A z_B = \frac{-1.683\,623\,642}{1.02} = -1.650\,611\,414$$

$$\boxed{z_A z_B = -1.65}$$

When rounded to a single significant figure,  $\boxed{z_A z_B = -2}$  which is in fact consistent with the statement given in the question.

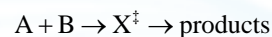
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**9.48.** Suppose that the rates of ionic reactions in solution were proportional to the activity rather than the concentration of activated complexes. Derive an equation relating the logarithm of the rate constant to the ionic strength and the charge numbers of the ions and contrast it with Eq. 9.124. Can the results in Figure 9.22 be reconciled with the equation you have derived?

**Solution:**

Let the following reaction occur as follows,



The basis of the ionic strength treatment is that the rate of a reaction is proportional to the concentration of the activated complexes,  $X^\ddagger$  and NOT to their activity. The rate equation is thus,

$$v = k [X^\ddagger]$$

The equilibrium between the activated complexes and the reactants A and B may then be expressed as,

$$K^\ddagger = \frac{a^\ddagger}{a_A a_B} = \frac{[X^\ddagger]}{[A][B]} \frac{\gamma^\ddagger}{\gamma_A \gamma_B} \quad (\text{Eq. 9.118})$$

Remember that  $a$  and  $b$  are the activities and  $\gamma$  represents the activity coefficient. We will now introduce Eq. 9.118 into a modified rate equation (from the one given above). Suppose that,

$$v = k [X^\ddagger] \gamma^\ddagger$$

$$[X^\ddagger] = K^\ddagger [A][B] \frac{\gamma_A \gamma_B}{\gamma^\ddagger}$$

$$v = k \left( K^\ddagger [A][B] \frac{\gamma_A \gamma_B}{\cancel{\gamma^\ddagger}} \right) \cancel{\gamma^\ddagger}$$

$$v = k K^\ddagger [A][B] \gamma_A \gamma_B$$

Let

$$kK = k_0 \text{ and } k = kK^\ddagger [A][B] \gamma_A \gamma_B$$

Taking the logarithm of each part of the equation, we obtain,

$$\log_{10} k = \log_{10} k_0 + \log_{10} \gamma_A \gamma_B$$

Using the fact that  $\log_{10} \gamma = -Bz^2 \sqrt{I}$  we can make a substitution to get,

$$\boxed{\log_{10} k = \log_{10} k_0 - B[z_A^2 + z_B^2] \sqrt{I}}$$

In this particular situation, plotting  $\log_{10} k$  against  $\sqrt{I}$  will always yield a line with a negative slope. This conclusion is inconsistent with the results presented in Figure 9.22.

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**9.49.** When the subatomic species muonium (Mu) was first discovered in 1960, it was not known whether it bore an electric charge. The answer was provided by a kinetic study of the ionic strength effect on the reaction  $\text{Mu} + \text{Cu}^{2+}$  in aqueous solution. The following rate constants were measured at two ionic strengths:

$$\begin{array}{ll} I = 0 \text{ M} & k = 6.50 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ I = 0.9 \text{ M} & k = 6.35 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{array}$$

Suppose that muonium had a single negative charge; what would  $k$  be expected to be at an ionic strength of 0.9 M? What do you deduce about the actual charge on muonium?

**Solution:**

If there were a single negative charge on the muonium ion, the slope of the plot of  $\log_{10} k$  against  $\sqrt{I}$  would yield a slope of approximately -2. Thus,  $z_A z_B = -2$ . According to Eq. 9.124,

$\log_{10} k = \log_{10} k_0 + 2Bz_A z_B \sqrt{I}$  which can be rearranged to obtain,

$$\log_{10} k - \log_{10} k_0 = 2Bz_A z_B \sqrt{I}$$

$$\log_{10} \left( \frac{k}{k_0} \right) = 1.02 \times (-2) \times (0.9)^{1/2} = -6.12$$

$$\left( \frac{k}{k_0} \right) = 10^{-6.12} = 7.59 \times 10^{-7} \text{ ???}$$

I have no clue what the previous author did here. There is absolutely no explanation as to where he got his numbers from. I cannot finish this problem.

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**9.50.** The rate constants of a second-order reaction in aqueous solution at 25 °C had the following values at two ionic strengths:

$I/\text{mol dm}^{-3}$	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$2.5 \times 10^{-3}$	$1.40 \times 10^{-3}$
$2.5 \times 10^{-2}$	$2.35 \times 10^{-3}$

Make an estimate of the value of  $z_A z_B$ , the product of the charge numbers.

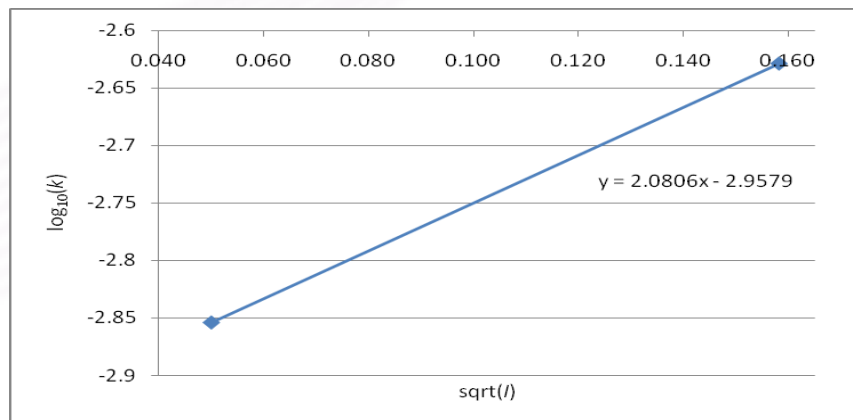
**Solution:**

Given: see above

Required: estimate  $z_A z_B$

Let us plot  $\log_{10} k$  against  $\sqrt{I}$ .

$I (10^{-3} \text{ mol dm}^{-3})$	$k (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$\text{sqrt}(I)$	$\log_{10}(k)$
2.50E-03	1.40E-03	0.05000	-2.8539
2.50E-02	2.35E-03	0.15811	-2.6289



Linear Regression Statistics			
<b>m</b>	2.080582256	-2.957901077	<b>b</b>
<b>Sm</b>	0	0	<b>Sb</b>
<b>R<sup>2</sup></b>	1	0	<b>Sy</b>
<b>F</b>	NA	0	<b>DF</b>

The slope of the plot above is equal to  $m = 2.080\,582\,256$ . This means that,

$$2.080\,582\,256 = 1.02 z_A z_B$$

$$z_A z_B = \frac{2.080\,582\,256}{1.02}$$

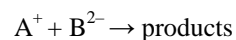
$$z_A z_B = 2.04$$

An approximation to one significant figure yields,  $z_A z_B \approx 2$ .

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**9.51.** A reaction of the type:



was found at 25 °C to have a rate constant of  $2.8 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at an ionic strength of  $1.0 \times 10^{-3} \text{ M}$ . Assume the Debye-Hückel limiting law to apply and estimate the rate constant at zero ionic strength.

**Solution:**

Given:  $k = 2.8 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $T = 25 \text{ °C}$ ,  $I = 1.0 \times 10^{-3} \text{ M}$

Required:  $k$  at  $I_0$  ( $k_0$ )

The Debye-Hückel limiting law states that,

$$\log_{10} k = \log_{10} k_0 + 2Bz_A z_B \sqrt{I}$$

This can be rearranged to solve for  $k_0$  upon substitution of the appropriate values.

$$\log_{10} k = \log_{10} k_0 + 2Bz_A z_B \sqrt{I}$$

$$\log_{10} k_0 = \log_{10} k - 2Bz_A z_B \sqrt{I}$$

$$\log_{10} k_0 = \log_{10} (2.8 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) - 1.02(-2)\sqrt{1.0 \times 10^{-3} \text{ M}}$$

$$\log_{10} k_0 = -3.552\ 842 + 0.064\ 510$$

$$\log_{10} k_0 = -3.488\ 332$$

$$k_0 = 10^{-3.488\ 332}$$

$$\boxed{k_0 = 3.25 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

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**9.52.** The rate of a reaction at 300 K is doubled when the pressure is increased from 1 bar to 2000 bar. Calculate  $\Delta^\ddagger V^\circ$ , assuming it to be independent of pressure.

**Solution:**

Given:  $T = 300 \text{ K}$ ,  $P_0 = 1 \text{ bar}$ ,  $P_f = 2000 \text{ bar}$

Required:  $\Delta^\ddagger V^\circ$  (pressure independent)

According to Eq. 9.129 we know that,  $\ln k = \ln k_0 - \frac{\Delta^\ddagger V^\circ}{RT} \Delta P$ .

We are told that the rate of the reaction increases 2-fold when the pressure is increased from 1 bar to 2000 bar. This would mean that,

$$v_1 = k_0$$

$$v_2 = k$$

$$\ln \frac{v_2}{v_1} = \ln 2 = \ln \frac{k}{k_0} = -\frac{\Delta^\ddagger V^\circ}{RT} \Delta P$$

$$\ln 2 = -\frac{\Delta^\ddagger V^\circ}{RT} \Delta P$$

Rearrange this expression to isolate  $\Delta^\ddagger V^\circ$ ,

$$\Delta^\ddagger V^\circ = \frac{-\ln 2(RT)}{P}$$

Substitution yields,

$$\Delta^\ddagger V^\circ = \frac{-0.693 \, 147 (8.3145 \, \text{J K}^{-1} \text{mol}^{-1}) (300 \, \text{K})}{(2000-1) \, \text{bar}}$$

$$\Delta^\ddagger V^\circ = -0.864 \, 908 \, \text{J bar}^{-1} \text{mol}^{-1}$$

$$1 \, \text{bar} = 10^5 \, \text{Pa}, 1 \, \text{atm} = 1.013 \, 25 \times 10^5 \, \text{Pa}, 1 \, \text{atm dm}^3 = 101.325 \, \text{J}$$

$$\Delta^\ddagger V^\circ = -0.864 \, 908 \, \cancel{\text{J}} \, \cancel{\text{bar}^{-1}} \, \text{mol}^{-1} \times \frac{1 \, \cancel{\text{bar}}}{10^5 \, \cancel{\text{Pa}}} \times \frac{1.013 \, 25 \times 10^5 \, \cancel{\text{Pa}}}{1 \, \cancel{\text{atm}}} \times \frac{1 \, \cancel{\text{atm}} \, \text{dm}^3}{101.325 \, \cancel{\text{J}}}$$

$$\Delta^\ddagger V^\circ = -8.649 \, 081 \times 10^{-3} \, \text{dm}^3 \text{mol}^{-1}$$

$$1 \text{ dm}^3 = 0.001 \text{ m}^3$$

$$\Delta^\ddagger V^\circ = -8.649\,081 \times 10^{-3} \cancel{\text{ dm}^3} \text{ mol}^{-1} \times \frac{0.001 \text{ m}^3}{1 \cancel{\text{ dm}^3}}$$

$$\boxed{\Delta^\ddagger V^\circ = -8.65 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}$$

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**9.53.** The following results were obtained for the solvolysis of benzyl chloride in an acetone-water solution at 25 °C:

$P/10^2 \text{ kPa}$	1.00	3.45	6.89	10.33
$k/10^{-6} \text{ s}^{-1}$	7.18	9.58	12.2	15.8

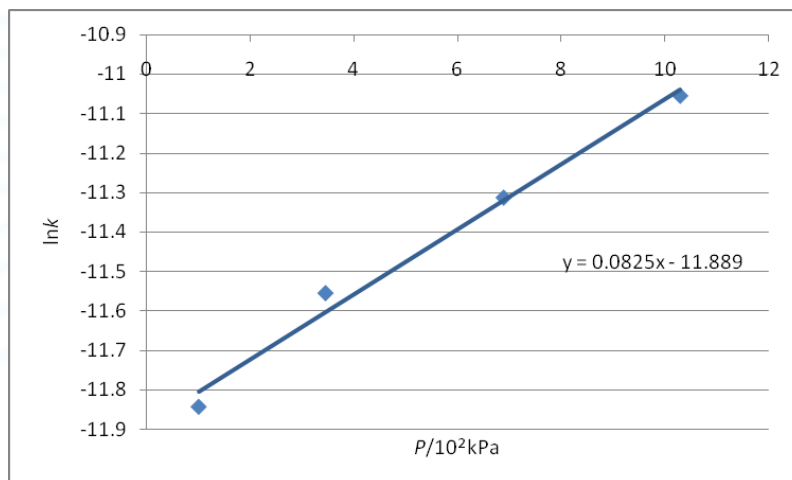
Make an appropriate plot and estimate  $\Delta^\ddagger V^\circ$ .

**Solution:**

Given: se above

Required: plot and estimate  $\Delta^\ddagger V^\circ$

$P/10^2 \text{ kPa}$	$k/10^{-6} \text{ s}^{-1}$	$\ln k$
1.00	7.18	-11.844
3.45	9.58	-11.556
6.89	12.2	-11.314
10.3	15.8	-11.056



Linear Regression Statistics			
<b>m</b>	7.58108E-06	-11.83434645	<b>b</b>
<b>Sm</b>	1.89127E-07	0.012186716	<b>Sb</b>
<b>R<sup>2</sup></b>	0.998756818	0.014547781	<b>Sy</b>
<b>F</b>	1606.774843	2	<b>DF</b>

According to Eq. 9.129 we know that,  $\ln k = \ln k_0 - \frac{\Delta^\ddagger V^\circ}{RT} P$ . This means that a plot of  $\ln k$  against  $P$  will yield a slope that is equal to  $-\frac{\Delta^\ddagger V^\circ}{RT}$ . This information will allow us to determine the value of  $\Delta^\ddagger V^\circ$ .

$$m = -\frac{\Delta^\ddagger V^\circ}{RT} = 7.581\,08 \times 10^{-6} \text{ kPa}^{-1} = 7.581\,08 \times 10^{-9} \text{ Pa}^{-1}$$

$$-\Delta^\ddagger V^\circ = 7.581\,08 \times 10^{-9} \text{ Pa}^{-1} \left( 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1} \times 298.15 \cancel{\text{K}} \right)$$

$$\Delta^\ddagger V^\circ = -1.879 \times 10^{-5} \text{ J Pa}^{-1} \text{ mol}^{-1}$$

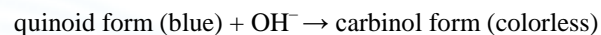
1 J Pa<sup>-1</sup> = 1 m<sup>3</sup> therefore,

$$\Delta^\ddagger V^\circ = -1.88 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

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**9.54.** The fading of bromphenol blue in alkaline solution is a second-order reaction between hydroxide ions and the quinoid form of the dye:



The following results show the variation of the second-order rate constant  $k$  with the hydrostatic pressure  $P$  at 25 °C:

$P/10^4 \text{ kPa}$	101.3	2.76	5.51	8.27	11.02
$k/10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	9.30	11.13	13.1	15.3	17.9

Estimate  $\Delta^\ddagger V^\circ$ .

**Solution:**

Given: second order:  $P/10^4 \text{ kPa}$  and  $k/10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  above

Required:  $\Delta^\ddagger V^\circ$

We will use the same method as we did in the previous problem. We should first begin by adjusting the units to simplify our results.

$$1 \text{ M} = 1 \text{ mol L}^{-1}$$

$$1 \text{ L} = 1 \text{ m}^3, 1 \text{ m}^3 = 1000 \text{ dm}^3$$

$$1 \text{ M} = 1 \text{ mol } \cancel{\text{L}^{-1}} \times \frac{1 \cancel{\text{L}}}{1 \cancel{\text{m}^3}} \times \frac{1 \cancel{\text{m}^3}}{1000 \text{ dm}^3}$$

$$1 \text{ M} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$(1 \text{ M})^{-1} = 1000 \text{ dm}^3 \text{ mol}^{-1}$$

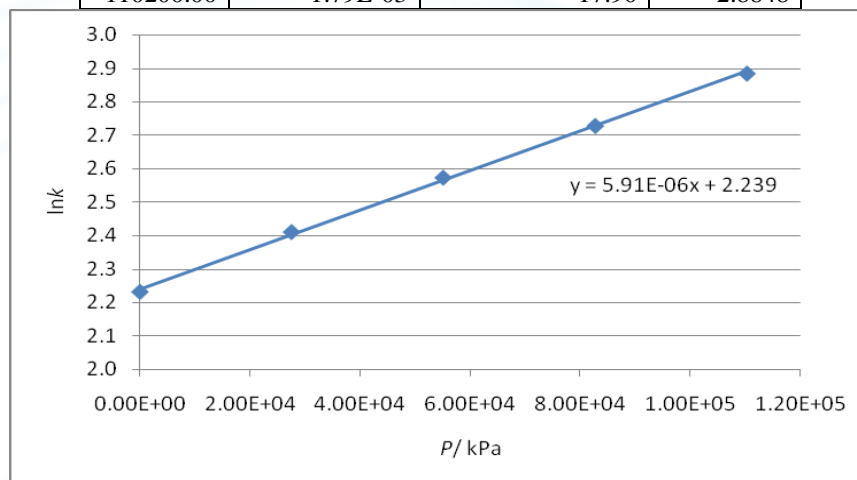
$$(10^{-4} \text{ M})^{-1} = 10\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ and } (10^{-4} \text{ M})^{-1} \text{ s}^{-1} = 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The rate constant can now be expressed in the following form,

$$k / 10^{-4} \text{ M}^{-1} \text{ s}^{-1} = k / 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$P / \text{kPa}$	$k / 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	$k / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\ln k$
1013000.00	9.30E-04	9.30	2.2300

27600.00	1.11E-03	11.13	2.4096
55100.00	1.31E-03	13.10	2.5726
82700.00	1.53E-03	15.30	2.7279
110200.00	1.79E-03	17.90	2.8848



linear regression statistics:	
5.9127E-06	2.238955304
1.0317E-07	0.006964007
0.99908744	0.008981709
3284.45091	3

According to Eq. 9.129 we know that,  $\ln k = \ln k_0 - \frac{\Delta^\ddagger V^\circ}{RT} P$ . This means that a plot of  $\ln k$  against  $P$  will yield a slope that is equal to  $-\frac{\Delta^\ddagger V^\circ}{RT}$ . This information will allow us to determine the value of  $\Delta^\ddagger V^\circ$ .

$$m = -\frac{\Delta^\ddagger V^\circ}{RT} = 5.9127 \times 10^{-9} \text{ Pa}^{-1}$$

$$-\Delta^\ddagger V^\circ = 5.9127 \times 10^{-9} \text{ Pa}^{-1} \left( 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1} \times 298.15 \cancel{\text{K}} \right)$$

$$\Delta^\ddagger V^\circ = -1.466 \times 10^{-5} \text{ J Pa}^{-1} \text{ mol}^{-1}$$

1 J Pa<sup>-1</sup> = 1 m<sup>3</sup> therefore,

$$\boxed{\Delta^\ddagger V^\circ = -1.47 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

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**9.55.** Use Figure 9.23 to make approximate estimates of the volumes of activation for the alkaline hydrolyses of methyl acetate, ethyl acetate, and propionamide, at 25 °C.

**Solution:**

Given: Figure 9.23,  $T = 25\text{ °C}$

Required: estimate  $\Delta^\ddagger V^\circ$  in each case

From Figure 9.23, at 10 000 lb per square inch, the values of  $\log_{10} \frac{k}{k_0}$  are:

Ethyl acetate: 0.105

Methyl acetate: 0.11

Propionamide: 0.20

The value of  $\log_{10} \frac{k}{k_0}$  when the pressure is 10 000 pounds per square inch is approximately 0.105. The slope of a plot in which natural logarithms were used would therefore be,

$$\ln \frac{k}{k_0} = \frac{2.303 \times 0.105}{10\,000 \text{ psi}}$$

1 psi =  $6.89 \times 10^3$  Pa therefore,

$$\ln \frac{k}{k_0} = \frac{2.303 \times 0.105}{10\,000 \cancel{\text{psi}} \times \frac{6.89 \times 10^3 \text{ Pa}}{1 \cancel{\text{psi}}}}$$

$$\ln \frac{k}{k_0} = \frac{2.303 \times 0.105}{10\,000 \times 6.89 \times 10^3 \text{ Pa}}$$

$$\log_{10} \frac{k}{k_0} = 3.509\,651 \times 10^{-9} \text{ Pa}^{-1}$$

According to Eq. 9.129 (for ethyl acetate),

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$$\ln k = \ln k_0 - \frac{\Delta^\ddagger V^\circ}{RT} P$$

$$\ln k - \ln k_0 = -\frac{\Delta^\ddagger V^\circ}{RT} P \rightarrow \ln \frac{k}{k_0} = -\frac{\Delta^\ddagger V^\circ}{RT} P \text{ since } mP = -\frac{\Delta^\ddagger V^\circ}{RT}$$

$$-\Delta^\ddagger V^\circ = 3.509\,651 \times 10^{-9} \text{ Pa}^{-1} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})$$

$$\Delta^\ddagger V^\circ = -8.69\,979 \times 10^{-6} \text{ J Pa}^{-1} \text{ mol}^{-1} \rightarrow \text{since } 1 \text{ J Pa}^{-1} = 1 \text{ m}^3 \text{ therefore,}$$

$$\boxed{\Delta^\ddagger V^\circ = -8.70 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}$$

Similarly, for methyl acetate;

$$\ln k = \ln k_0 - \frac{\Delta^\ddagger V^\circ}{RT} P$$

$$\ln k - \ln k_0 = -\frac{\Delta^\ddagger V^\circ}{RT} P \rightarrow \ln \frac{k}{k_0} = -\frac{\Delta^\ddagger V^\circ}{RT} \cancel{P} \text{ since } m = -\frac{\Delta^\ddagger V^\circ}{RT}$$

$$-\Delta^\ddagger V^\circ = 3.68 \times 10^{-9} \text{ Pa}^{-1} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})$$

$$\Delta^\ddagger V^\circ = -9.122\,602\,884 \times 10^{-6} \text{ J Pa}^{-1} \text{ mol}^{-1} \rightarrow \text{since } 1 \text{ J Pa}^{-1} = 1 \text{ m}^3 \text{ therefore,}$$

$$\boxed{\Delta^\ddagger V^\circ = -9.12 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}$$

For proprionamide the slope is;

$$\ln k = \ln k_0 - \frac{\Delta^\ddagger V^\circ}{RT} P$$

$$\ln k - \ln k_0 = -\frac{\Delta^\ddagger V^\circ}{RT} P \rightarrow \ln \frac{k}{k_0} = -\frac{\Delta^\ddagger V^\circ}{RT} \cancel{P} \text{ since } m = -\frac{\Delta^\ddagger V^\circ}{RT}$$

$$-\Delta^\ddagger V^\circ = 6.685 \times 10^{-9} \text{ Pa}^{-1} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})$$

$$\Delta^\ddagger V^\circ = -1.657\,190\,225 \times 10^{-5} \text{ J Pa}^{-1} \text{ mol}^{-1} \rightarrow \text{since } 1 \text{ J Pa}^{-1} = 1 \text{ m}^3 \text{ therefore,}$$

$$\boxed{\Delta^\ddagger V^\circ = -1.66 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$



[Back to Problem 9.55](#)

[Back to Top](#)

CHAPTER

# 10

Chemical Kinetics II.  
Composite Mechanisms

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**Physical Chemistry**

Electronic Edition

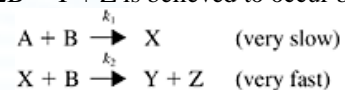
Publisher: MCH Multimedia Inc.

**Problems and Solutions**

## Chapter 10

## Composite Mechanisms and Rate Equations

10.1. Suppose that a reaction of stoichiometry  $A + 2B = Y + Z$  is believed to occur by the mechanism:

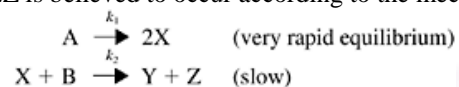


Where X is an intermediate. Write the expression for the rate of formation of Y.

[Solution](#)

Field Code Changed

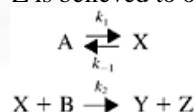
10.2. Suppose that a reaction  $A + 2B = 2Y + 2Z$  is believed to occur according to the mechanism:



Obtain an expression for the rate of formation of the product Y.

[Solution](#)

10.3. Suppose that a reaction of stoichiometry  $A + B = Y + Z$  is believed to occur according to the mechanism:

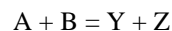


Apply the steady-state treatment and obtain an expression for the rate. To what expressions does the general rate equation reduce if;

- The second reaction is slow, the initial equilibrium being established very rapidly?
- The second reaction is very rapid compared with the first reaction in either direction?

[Solution](#)

10.4. A reaction of stoichiometry:



is found to be second order in A and zero order in B. Suggest a mechanism that is consistent with this behavior.

[Solution](#)

- 10.5.** The rate of formation of the product of a reaction is found to give a nonlinear Arrhenius plot, the line being convex to the  $1/T$  axis (i.e., the activation energy is higher at higher temperatures). Suggest a reason for this type of behavior.  
(Hint: For this and the following problem, consider the possibility of two parallel reactions and of two consecutive reactions having different activation energies.)

[Solution](#)

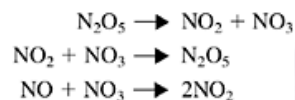
- 10.6.** An Arrhenius plot is concave to the  $1/T$  axis (i.e., it exhibits a lower activation energy at higher temperatures). Suggest a reason for this type of behavior.

[Solution](#)

- 10.7.** Nitrogen pentoxide reacts with nitric oxide in the gas phase according to the stoichiometric equation:



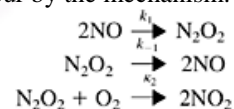
The following mechanism has been proposed:



Assume that the steady-state treatment can be applied to  $\text{NO}_3$ , and derive an equation for the rate of consumption of  $\text{N}_2\text{O}_5$ .

[Solution](#)

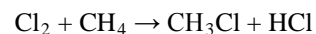
- 10.8.** The reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  is believed to occur by the mechanism:



Assume  $\text{N}_2\text{O}_2$  to be in a steady state and derive the rate equation. Under what conditions does the rate equation reduce to second-order kinetics in NO and first-order kinetics in  $\text{O}_2$ ?

[Solution](#)

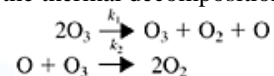
- \*10.9.** The gas-phase reaction:



proceeds by a free-radical chain reaction in which the chain propagators are Cl and  $\text{CH}_3$  (but not H), and the chain-ending step is  $2\text{Cl} \rightarrow \text{Cl}_2$ . Write the mechanism, identify the initiation reaction and the chain-propagating steps, and obtain an expression for the rate of the overall reaction.

[Solution](#)

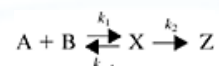
**10.10.** The following mechanism has been proposed for the thermal decomposition of pure ozone in the gas phase:



Derive the rate equation.

[Solution](#)

**\*10.11.** A reaction occurs by the mechanism:



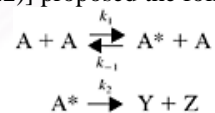
and the concentration of X is sufficiently small compared with the concentrations of A and B that the steady-state treatment applies. Prove that the activation energy  $E_a$  at any temperature is given by:

$$E_a = \frac{k_{-1}(E_1 + E_2 - E_{-1}) + k_2 E_1}{k_{-1} + k_2}$$

that is, is the weighted mean of the values  $E_1 + E_2 - E_{-1}$ , and  $E_1$ , which apply, respectively, to the limiting cases of  $k_1 \gg k_2$  and  $k_2 \gg k_{-1}$ .

[Solution](#)

**10.12.** F. A. Lindemann [*Trans. Faraday Soc.*, 17, 598(1922)] proposed the following mechanism for a unimolecular gas reaction:



The species  $\text{A}^*$  is an energized molecule that is present in low concentrations. Apply the steady-state treatment to  $\text{A}^*$  and obtain an expression for the rate in terms of  $[\text{A}]$ ,  $k_1$ ,  $k_{-1}$ , and  $k_2$ . Show that the mechanism predicts first-order kinetics at higher A concentrations and second-order kinetics at lower ones.

[Solution](#)

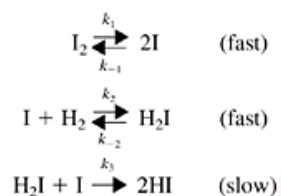
**\*10.13.** Certain polymerizations involve esterification reactions between  $\text{-COOH}$  groups on one molecule and  $\text{-OH}$  groups on another. Suppose that the concentration of such functional groups is  $c$  and that the rate of their removal by esterification obeys the equation:

$$-\frac{dc}{dt} = kc^2$$

Obtain an equation relating the time  $t$  to the fraction  $f$  of functional groups remaining and to the initial concentration  $c_0$  of functional groups.

[Solution](#)

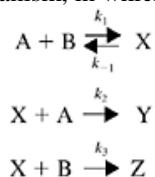
**\*10.14.** Show that the mechanism:



leads to the result that the rate equation for the overall reaction is  $v = k[\text{H}_2][\text{I}_2]$ .

[Solution](#)

**10.15.** Apply the steady-state treatment to the following mechanism, in which Y and Z are final products and X is a labile intermediate:



Obtain an expression for the rate of formation of the product Z. What rate equations are obtained if (a) A and (b) B are present in great excess?

[Solution](#)

**Photochemistry and Radiation Chemistry**

- 10.16.** Calculate the maximum wavelength of the radiation that will bring about dissociation of a diatomic molecule having a dissociation energy of  $390.4 \text{ kJ mol}^{-1}$ .

[Solution](#)

- 10.17.** Hydrogen iodide undergoes decomposition into  $\text{H}_2 + \text{I}_2$  when irradiated with radiation having a wavelength of 207 nm. It is found that when 1 J of energy is absorbed,  $440 \mu\text{g}$  of HI is decomposed. How many molecules of HI are decomposed by 1 photon of radiation of this wavelength? Suggest a mechanism that is consistent with this result.

[Solution](#)

- 10.18.** A 100-watt mercury-vapor lamp emits radiation of 253.7 nm wavelength and may be assumed to operate with 100% efficiency. If all the light emitted is absorbed by a substance that is decomposed with a quantum yield of unity, how long will it take for 0.01 mol to be decomposed?

[Solution](#)

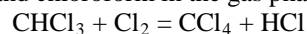
- 10.19.** Suppose that the radiation emitted by the lamp in Problem 10.18 is all absorbed by ethylene, which decomposes into  $\text{C}_2\text{H}_2 + \text{H}_2$  with a quantum yield of unity. How much ethyne will be produced per hour?

[Solution](#)

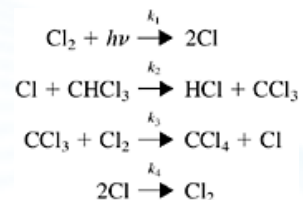
- 10.20.** A 1000-watt mercury vapor flash lamp emits radiation of 253.7 nm wavelength, and the duration of the flash is  $1 \mu\text{s}$ . Suppose that all of the radiation of a single flash is absorbed by mercury vapor; how many atoms of excited mercury are formed?

[Solution](#)

**\*10.21.** The photochemical reaction between chlorine and chloroform in the gas phase follows the stoichiometric equation:



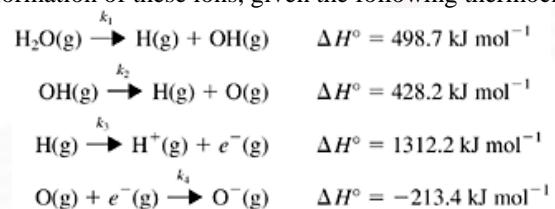
It is believed to occur by the mechanism:



Assume the rate of formation of Cl atoms in the initiation reaction to be  $2I_a$ , where  $I_a$  is the intensity of light absorbed, and obtain an expression for the overall rate in terms of  $I_a$  and  $[\text{CHCl}_3]$ .

[Solution](#)

**\*10.22.** When water vapor is irradiated with a beam of high-energy electrons, various ions such as  $\text{H}^+$  and  $\text{O}^-$  appear. Calculate the minimum energies required for the formation of these ions, given the following thermochemical data:

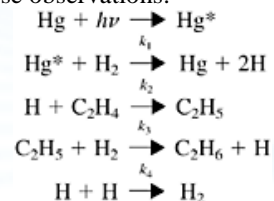


Are the results you obtain consistent with the experimental appearance potentials of 19.5 eV for  $\text{H}^+$  and 7.5 eV for  $\text{O}^-$ ?

[Solution](#)



- 10.23.** The mercury-photosensitized hydrogenation of ethylene in the presence of mercury vapor is first-order with respect to ethylene and half-order with respect to  $H_2$ . Its rate is proportional to the square root of the intensity of the light absorbed. The following mechanism has been suggested to account for these observations:



Applying the steady-state approximation to  $[\text{H}]$  and  $[\text{C}_2\text{H}_5]$ , verify that the mechanism indeed supports the observations. What is the observed rate constant in terms of the rate constants of the elementary reactions?

[Solution](#)

#### Catalysis

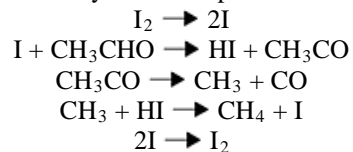
- 10.24.** The hydrolysis of a substance is specifically catalyzed by hydrogen ions, and the rate constant is given by:

$$k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1} = 4.7 \times 10^{-2} ([\text{H}^+]/\text{mol dm}^{-3})$$

When the substance was dissolved in a  $10^{-3} M$  solution of an acid HA, the rate constant was  $3.2 \times 10^{-5} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . Calculate the dissociation constant of HA.

[Solution](#)

- \*10.25.** The following is a slightly simplified version of the mechanism proposed in 1937 by G. K. Rollefson and R. F. Faull [*J. Amer. Chem. Soc.*, 59, 625(1937)] to explain the iodine-catalyzed decomposition of acetaldehyde:



Apply the steady-state treatment to I,  $\text{CH}_3\text{CO}$ , and  $\text{CH}_3$  and obtain an expression for the rate.

[Solution](#)

**\*10.26.** Suppose that a reaction is catalyzed by a series of homologous acids and that the Hammett equation (9.130) applies:

$$\log_{10} k_a = \log_{10} k_0 + \sigma \rho$$

where  $\sigma$  is the substituent constant and  $\rho$  is the reaction constant. Suppose that the corresponding equation for the dissociation of the acid is:

$$\log_{10} K_a = \log_{10} K_0 + \sigma \rho''$$

where  $\rho'$  is the reaction constant for the dissociation; the substituent constants are the same in both equations. Prove that the Brønsted equation:

$$k_a = G_a K_a^\alpha$$

applies. How does  $\alpha$  relate to the reaction constants  $\rho$  and  $\rho'$ ?

[Solution](#)

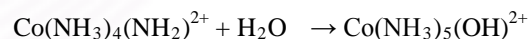
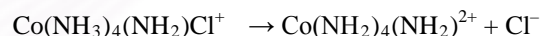
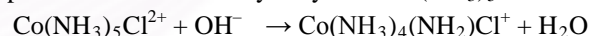
**10.27.** The hydrolysis of ethyl acetate catalyzed by hydrochloric acid obeys the rate equation:

$$v = k[\text{ester}][\text{HCl}]$$

and the reaction essentially goes to completion. At 25 °C the rate constant is  $2.80 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . What is the half-life of the reaction if  $[\text{ester}] = 0.1 \text{ M}$  and  $[\text{HCl}] = 0.01 \text{ M}$ ?

[Solution](#)

**10.28.** The following mechanism has been proposed for the alkaline hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ :



Assume  $\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}^+$  and  $\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+}$  to be in the steady state and derive an expression for the rate of reaction.

Experimentally, the rate is proportional to  $[\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}] [\text{OH}^-]$ ; does this fact tell us anything about the relative magnitudes of the rate constants?

[Solution](#)

**10.29.** Confirm that Eq. 10.68,

$$[\text{H}^+]_{\min} = (k_{\text{OH}^-} K_w / k_{\text{H}^+})^{\frac{1}{2}}$$

follows from Eq. 10.66,

$$k = k_0 + k_{\text{H}^+} [\text{H}^+] + \frac{k_{\text{OH}^-} K_w}{[\text{H}^+]}$$

[Solution](#)

**10.30.** The following results have been obtained by D. B. Dahlberg and F. A. Long [*J. Amer. Chem. Soc.*, 95, 3825(1973)] for the base-catalyzed enolization of 3-methyl acetone.

Catalyst	$\text{ClCH}_2\text{COO}^-$	$\text{CH}_3\text{COO}^-$	$\text{HPO}_4^{2-}$
$K_a/\text{mol dm}^{-3}$	$1.39 \times 10^{-3}$	$1.80 \times 10^{-5}$	$6.25 \times 10^{-8}$
$k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$1.41 \times 10^{-3}$	$1.34 \times 10^{-2}$	0.26

Estimate the Brønsted coefficient  $\beta$ .

[Solution](#)

**10.31.** Suggest a plausible mechanism for the bromination of acetone catalyzed by hydroxide ions. As with the acid-catalyzed reaction discussed in Section 10.9, the rate is independent of the bromine concentration.

[Solution](#)

**10.32.** It was found by J. Halpern and coworkers [*J. Phys. Chem.*, 60, 1455(1956)] that the rate equation for the oxidation of molecular hydrogen by dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) catalyzed by  $\text{Cu}^{2+}$  ions is of the form:

$$v = \frac{k[\text{H}_2][\text{Cu}^{2+}]^2}{[\text{H}_2] + k'[\text{Cu}^{2+}]}$$

(\*\*Note that the rate is independent of the concentration of dichromate ions.)

Suggest a mechanism consistent with this behavior, and apply the steady-state treatment to obtain the rate expression. Comment on rate-controlling steps corresponding to special cases of the mechanism.

[Solution](#)

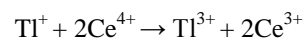
- 10.33.** For the oxidation of molecular hydrogen by dichromate ions catalyzed by  $\text{Ag}^+$  ions, A. H. Webster and J. Halpern [*J. Phys. Chem.*, 60, 280(1956)] obtained the rate equation:

$$\nu = k[\text{H}_2][\text{Ag}^+]^2 + \frac{k'[\text{H}_2][\text{Ag}^+]^2}{[\text{H}_2] + k''[\text{Ag}^+]}$$

The existence of two terms suggests that two mechanisms are occurring in parallel. Suggest the two mechanisms, applying the steady-state treatment to obtain the second term in the rate equation.

[Solution](#)

- 10.34.** The reaction:



is catalyzed by  $\text{Ag}^+$  ions. Under certain conditions the rate is proportional to  $[\text{Ce}^{4+}][\text{Ti}^+][\text{Ag}^+]/[\text{Ce}^{3+}]$

Suggest a mechanism consistent with this behavior.

[Solution](#)

**Enzyme-Catalyzed Reactions**

**10.35.** The following rates have been obtained for an enzyme-catalyzed reaction at various substrate concentrations:

$10^3[\text{S}]/\text{mol dm}^3$	Rate, $v$ /(arbitrary units)
0.4	2.41
0.6	3.33
1.0	4.78
1.5	6.17
2.0	7.41
3.0	8.70
4.0	9.52
5.0	10.5
10.0	12.5

Plot  $v$  against  $[\text{S}]$ ,  $1/v$  against  $1/[\text{S}]$ , and  $v/[\text{S}]$  against  $v$ , and from each plot estimate the Michaelis constant. Which plot appears to give the most reliable value?

[Solution](#)

**10.36.** The following data have been obtained for the myosin-catalyzed hydrolysis of ATP, at 25 °C and pH 7.0.

$10^5[\text{ATP}]/\text{mol dm}^{-3}$	$10^6v/\text{mol dm}^{-3} \text{ s}^{-1}$
7.5	0.067
12.5	0.095
20.0	0.119
32.5	0.149
62.5	0.185
155.0	0.191
320.0	0.195

Plot  $v$  against  $[S]$ ,  $1/v$  against  $1/[S]$ , and  $v/[S]$  against  $v$ , and from each plot calculate the Michaelis constant  $K_m$  and the limiting rate  $V$ .

[Solution](#)

**\*10.37.** The following values of  $V$  (limiting rate at high substrate concentrations) and  $K_m$  have been obtained at various temperatures for the hydrolysis of acetylcholine bromide, catalyzed by acetylcholinesterase.

$T/^{\circ}\text{C}$	$10^6 V / \text{mol dm}^{-3} \text{ s}^{-1}$	$K_m \times 10^4 / \text{mol dm}^{-3}$
20.0	1.84	4.03
25.0	1.93	3.75
30.0	2.04	3.35
35.0	2.17	3.05

- Assuming the enzyme concentration to be  $1.00 \times 10^{-11} \text{ mol dm}^{-3}$ , calculate the energy of activation, the enthalpy of activation, the Gibbs energy of activation, and the entropy of activation for the breakdown of the enzyme-substrate complex at  $25^{\circ}\text{C}$ .
- Assuming  $K_m$  to be the dissociation constant  $k_{-1}/k_1$  for the enzyme-substrate complex ( $\text{ES} \xrightleftharpoons[k_1]{k_{-1}} \text{E} + \text{S}$ ), determine the following thermodynamic quantities for the *formation* of the enzyme-substrate complex at  $25^{\circ}\text{C}$ :  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ .
- From the results obtained in parts (a) and (b), sketch a Gibbs energy diagram and an enthalpy diagram for the reaction.

[Solution](#)

**\*10.38.** The following data relate to an enzyme reaction:

$10^3[\text{s}]/\text{mol dm}^3$	$10^5 V/\text{mol dm}^3 \text{s}^{-1}$
2.0	13
4.0	20
8.0	29
12.0	33
16.0	36
20.0	38

The concentration of the enzyme is  $2.0 \text{ g dm}^{-3}$ , and its molecular weight is 50 000. Calculate  $K_m$ , the maximum rate  $V$ , and  $k_c$ .

[Solution](#)

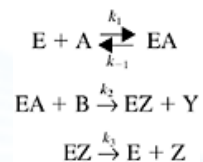
**10.39.** The following data have been obtained for the myosin-catalyzed hydrolysis of ATP.

Temperature/ $^{\circ}\text{C}$	$k_c \times 10^6/\text{s}^{-1}$
39.9	4.67
43.8	7.22
47.1	10.0
50.2	13.9

Calculate, at  $40^{\circ}\text{C}$ , the energy of activation, the enthalpy of activation, the Gibbs energy of activation, and the entropy of activation.

[Solution](#)

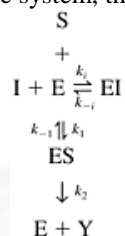
**\*10.40.** The following is a simplified version of the mechanism that has been proposed by H. Theorell and Britton Chance for certain enzyme reactions involving two substrates A and B.



Assume that the substrates A and B are in excess of E so that the steady-state treatment can be applied to EA and EZ, and obtain an expression for the rate.

[Solution](#)

**\*10.41.** When an inhibitor I is added to a single-substrate enzyme system, the mechanism is sometimes:



This is known as a *competitive* mechanism, since S and I compete for sites on the enzyme.

**a.** Assume that the substrate and inhibitor are present in great excess of the enzyme, apply the steady-state treatment, and obtain the rate equation.

**b.** Obtain an expression for the degree of inhibition defined as:

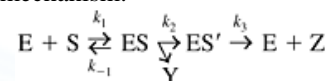
$$\epsilon = \frac{v_0 - v}{v_0}$$

where  $v$  is the rate in the presence of inhibitor and  $v_0$  is the rate in its absence.

[Solution](#)



\*10.42. Obtain the rate equation corresponding to the mechanism:



Assume ES and ES' to be in the steady state and the substrate concentration to be much higher than the enzyme concentration. Express the catalytic constant  $k_c$  and the Michaelis constant  $K_m$  in terms of  $k_1$ ,  $k_{-1}$ ,  $k_2$ , and  $k_3$ .

[Solution](#)

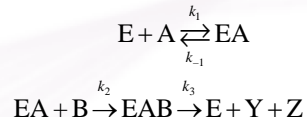
\*10.43. Enzyme-catalyzed reactions frequently follow an equation of the form of Eq. 10.85. Suppose that  $k_c$  and  $K_m$  show the following temperature dependence:

$$k_c = A_c \exp(-E_c/RT) \text{ and } K_m = B \exp(-\Delta H_m/RT)$$

where  $A_c$ ,  $B$ ,  $E_c$ , and  $\Delta H_m$  are temperature-independent parameters. Explain under what conditions, with  $[\text{S}]$  held constant, the rate may pass through a maximum as the temperature is raised.

[Solution](#)

10.44. Some enzyme reactions involving two substrates A and B occur by the following mechanism:

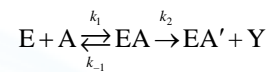


(This is known as the *ordered ternary-complex mechanism*; A must add first to E, and the resulting complex EA reacts with B; the complex EB is not formed.)

The concentrations of A and B are much greater than the concentration of E. Apply the steady-state treatment and obtain an expression for the rate.

[Solution](#)

- 10.45.** The following “ping-pong” mechanism appears sometimes to apply to an enzyme-catalyzed reaction between two substrates A and B to give the final products Y and Z:



It can be assumed that the substrates are present in great excess of the enzyme and that steady-state conditions apply. Obtain an expression for the rate of reaction.

[Solution](#)

### Polymerization

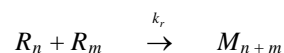
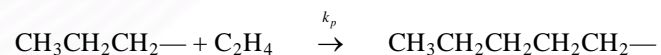
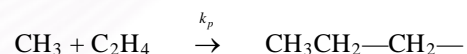
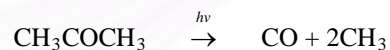
- 10.46.** The polymerization of styrene [M] catalyzed by benzoyl peroxide [C] obeys a kinetic equation of the form:

$$-\frac{d[M]}{dt} = k[M]^{3/2}[C]^{1/2}$$

Obtain an expression for the kinetic chain length, in terms of [M], [C], and the rate constants for initiation, propagation, and termination.

[Solution](#)

- 10.47.** The polymerization of ethylene [M] photosensitized by acetone occurs by the mechanism:



where one quantum gives  $2CH_3$ .

Show that the rate equation is:

$$-\frac{d[M]}{dt} = k_p \left( \frac{2I}{k_t} \right)^{1/2} [M]$$

where  $I$  is the intensity of light absorbed and  $k_p$  and  $k_t$  are the rate constants for the propagation and termination steps, respectively.

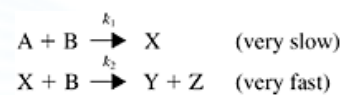
[Solution](#)

**Essay Questions**

- 10.48.** Explain the essential features of a chain reaction.
- 10.49.** Give an account of catalysis by acids and bases, distinguishing between specific and general catalysts.
- 10.50.** Will the rate of an enzyme-catalyzed reaction usually be more sensitive to temperature than that of the same reaction when it is uncatalyzed? Discuss.
- 10.51.** Explain how you would determine the parameters  $K_m$  and  $k_c$  for an enzyme reaction involving a single substrate.
- 10.52.** Explain clearly the difference between collisions and encounters. What significance does this distinction have in chemical kinetics?
- 10.53.** Explain clearly the kind of reasoning involved in deciding what might be the rate-controlling step in a chemical reaction.
- 10.54.** Give a qualitative description of the electronic double-layer theories of Helmholtz, Gouy and Chapman, and Stern.

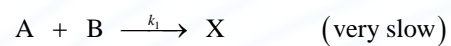
**Solutions**

**10.1.** Suppose that a reaction of stoichiometry  $A + 2B = Y + Z$  is believed to occur by the mechanism:



Where X is an intermediate. Write the expression for the rate of formation of Y.

**Solution:**



Because the second reaction is very fast, X is consumed once produced. So steady state approximation may be applied.

$$\frac{d[X]}{dt} = v_X = k_1[A][B] - k_2[X][B] = 0$$

$$[X] = \frac{k_1[A][\cancel{B}]}{k_2[\cancel{B}]}$$

$$[X] = \frac{k_1[A]}{k_2}$$

Similarly

$$\frac{d[Y]}{dt} = v_Y = k_2[X][B]$$

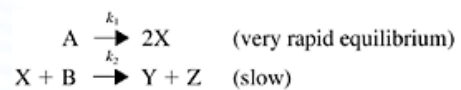
$$\frac{d[Y]}{dt} = \frac{k_1 \cancel{k_2} [A][B]}{\cancel{k_2}}$$

$$\frac{d[Y]}{dt} = k_1[A][B]$$

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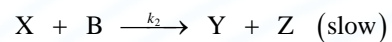
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**10.2.** Suppose that a reaction  $A + 2B = 2Y + 2Z$  is believed to occur according to the mechanism:

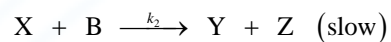


Obtain an expression for the rate of formation of the product Y.

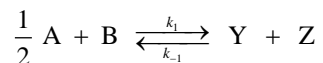
**Solution:**



Adjust for the stoichiometric coefficients, we can write the reactions as follows:



The overall reaction becomes:



Let us write out the rate of formation for substance X and Y.

$$\frac{d[X]}{dt} = k_1[A]^{1/2} - k_{-1}[X] - k_2[X][B]$$

$$\frac{d[Y]}{dt} = k_2[X][B]$$

Since X is an intermediate, steady state approximation can be applied.

$$\frac{d[X]}{dt} = k_1[A]^{1/2} - k_{-1}[X] - k_2[X][B] = 0$$

$$k_1[A]^{1/2} = k_{-1}[X] + k_2[X][B]$$

$$k_1[A]^{1/2} = [X](k_{-1} + k_2[B])$$

$$[X] = \frac{k_1[A]^{1/2}}{k_{-1} + k_2[B]}$$

Plug the above expression into the expression for the rate of formation of Y

$$\frac{d[Y]}{dt} = k_2[X][B]$$

$$\frac{d[Y]}{dt} = \frac{k_2 k_1 [A]^{1/2} [B]}{k_{-1} + k_2 [B]}$$

In this particular reaction, since the first step reaches equilibrium very rapidly, it is safe to assume that  $k_1 \gg k_2$ .

$$\frac{d[Y]}{dt} = \frac{k_2 k_1 [A]^{1/2} [B]}{k_{-1} + \cancel{k_2 [B]}}$$

$$\boxed{\frac{d[Y]}{dt} = v_Y = k_2 \left( \frac{k_1}{k_{-1}} \right) [A]^{1/2} [B]}$$

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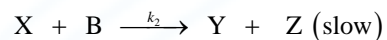
**10.3.** Suppose that a reaction of stoichiometry  $A + B = Y + Z$  is believed to occur according to the mechanism:



Apply the steady-state treatment and obtain an expression for the rate. To what expressions does the general rate equation reduce if;

- The second reaction is slow, the initial equilibrium being established very rapidly?
- The second reaction is very rapid compared with the first reaction in either direction?

**Solution:**



We will begin by writing out the rate of formation and consumption for each species involved.

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[X]$$

$$\frac{d[X]}{dt} = k_1[A] - k_{-1}[X] - k_2[X][B]$$

$$-\frac{d[B]}{dt} = k_2[X][B]$$

$$\frac{d[Y]}{dt} = k_2[X][B]$$

$$\frac{d[Z]}{dt} = k_2[X][B]$$

According to the steady-state treatment, we can assume that  $\frac{d[X]}{dt} = 0$  to a good approximation. This will enable us to find an expression for  $[X]$ .

$$k_1[A] = k_{-1}[X] + k_2[X][B]$$

$$k_1[A] = [X](k_{-1} + k_2[B])$$

$$[X] = \frac{k_1[A]}{(k_{-1} + k_2[B])}$$

- a) The information above leads us to believe that  $k_{-1} \gg k_2$  which means that,

$$[X] = \frac{k_1[A]}{(k_{-1} + k_2[B])}$$

$$v_Y = k_2 \left[ \frac{k_1[A]}{(k_{-1} + k_2[B])} \right] [B]$$

$$v_Y = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2[B]} \text{ this term can be dropped}$$

$$v_Y = \frac{k_1 k_2 [A][B]}{k_{-1}}$$

- b) The information above leads us to believe that  $k_2 \gg k_{-1}$  which means that,



$$[X] = \frac{k_1[A]}{(k_{-1} + k_2[B])}$$

$$v_Y = k_2 \left[ \frac{k_1[A]}{(k_{-1} + k_2[B])} \right] [B]$$

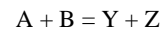
$$v_Y = \frac{k_1 k_2 [A][B]}{\cancel{k_{-1}} + k_2[B]} \text{ this term can be dropped}$$

$$v_Y = \frac{k_1 \cancel{k_2} [A] \cancel{[B]}}{\cancel{k_2} [B]}$$

$$\boxed{v_Y = k_1[A]}$$

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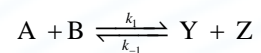
**10.4.** A reaction of stoichiometry:



is found to be second order in A and zero order in B. Suggest a mechanism that is consistent with this behavior.

**Solution:**

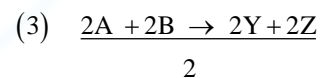
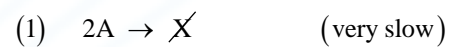
Given that,



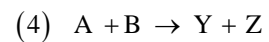
$$\nu = K[A]^2[B]^0 \text{ since } [B]^0 = 1 \text{ then,}$$

$$\nu = K[A]^2$$

This means that substance B should not appear in the rate determining step.



2



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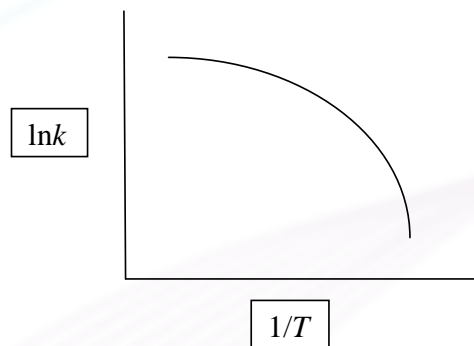
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- 10.5.** The rate of formation of the product of a reaction is found to give a nonlinear Arrhenius plot, the line being convex to the  $1/T$  axis (i.e., the activation energy is higher at higher temperatures). Suggest a reason for this type of behavior.  
(*Hint:* For this and the following problem, consider the possibility of two parallel reactions and of two consecutive reactions having different activation energies.)

**Solution:**

We are told that a plot of  $\ln k$  against  $1/T$  produces a non-linear curve that is convex to the  $x$ -axis. The following diagram is a sketch of what this would look like.

Based on the information given above, we can assume that two reactions are occurring simultaneously and that there is competition for a particular reactant.



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**10.6.** An Arrhenius plot is concave to the  $1/T$  axis (i.e., it exhibits a lower activation energy at higher temperatures). Suggest a reason for this type of behavior.

**Solution:**

Two consecutive reactions may be taking place here.

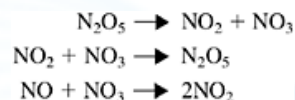
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**10.7.** Nitrogen pentoxide reacts with nitric oxide in the gas phase according to the stoichiometric equation:



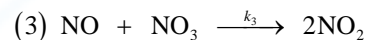
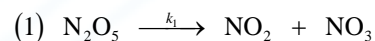
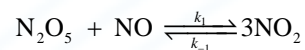
The following mechanism has been proposed:



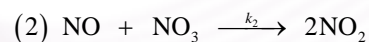
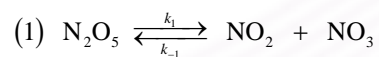
Assume that the steady-state treatment can be applied to  $\text{NO}_3$ , and derive an equation for the rate of consumption of  $\text{N}_2\text{O}_5$ .

**Solution:**

Let us begin by writing out the rate of formation and consumption for each species involved in the reaction.



Since the first two equations can be combined to a single equilibrium, we can write,



$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = v_{\text{N}_2\text{O}_5} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3]$$

$$\frac{d[\text{NO}_3]}{dt} = v_{\text{NO}_3} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{NO}_3]$$

$$-\frac{d[\text{NO}]}{dt} = v_{\text{NO}} = k_3[\text{NO}][\text{NO}_3]$$

According to the steady-state approximation,

$$\frac{d[\text{NO}_3]}{dt} = v_{\text{NO}_3} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}][\text{NO}_3] = 0$$

$$k_1[\text{N}_2\text{O}_5] = k_{-1}[\text{NO}_2][\text{NO}_3] + k_2[\text{NO}][\text{NO}_3]$$

$$k_1[\text{N}_2\text{O}_5] = [\text{NO}_3](k_{-1}[\text{NO}_2] + k_2[\text{NO}])$$

$$[\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{(k_{-1}[\text{NO}_2] + k_2[\text{NO}])}$$

This can be substituted into the rate of consumption for  $[\text{N}_2\text{O}_5]$  and simplified.

$$v_{\text{N}_2\text{O}_5} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3]$$

$$v_{\text{N}_2\text{O}_5} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2] \left( \frac{k_1[\text{N}_2\text{O}_5]}{(k_{-1}[\text{NO}_2] + k_2[\text{NO}])} \right)$$

$$v_{\text{N}_2\text{O}_5} = k_1[\text{N}_2\text{O}_5] - \frac{k_1 k_{-1} [\text{NO}_2][\text{N}_2\text{O}_5]}{(k_{-1}[\text{NO}_2] + k_2[\text{NO}])}$$

$$v_{\text{N}_2\text{O}_5} = \frac{k_1[\text{N}_2\text{O}_5](k_{-1}[\text{NO}_2] + k_2[\text{NO}]) - k_1 k_{-1} [\text{NO}_2][\text{N}_2\text{O}_5]}{(k_{-1}[\text{NO}_2] + k_2[\text{NO}])}$$

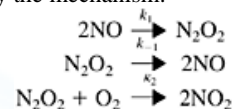
$$v_{\text{N}_2\text{O}_5} = \frac{k_1 k_{-1} [\text{NO}_2][\text{N}_2\text{O}_5] + k_1 k_2 [\text{N}_2\text{O}_5][\text{NO}] - k_1 k_{-1} [\text{NO}_2][\text{N}_2\text{O}_5]}{(k_{-1}[\text{NO}_2] + k_2[\text{NO}])}$$

$$v_{\text{N}_2\text{O}_5} = \frac{k_1 k_2 [\text{N}_2\text{O}_5][\text{NO}]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]}$$

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**10.8.** The reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  is believed to occur by the mechanism:

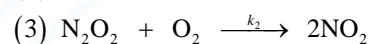
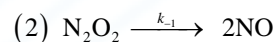
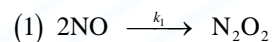
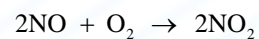


Assume  $\text{N}_2\text{O}_2$  to be in a steady state and derive the rate equation. Under what conditions does the rate equation reduce to second-order kinetics in NO and first-order kinetics in  $\text{O}_2$ ?

**Solution:**

Given: see above

Required: Under what conditions does the rate equation reduce to second-order kinetics in NO and first-order kinetics in  $\text{O}_2$ ?



$$\frac{d[\text{NO}_2]}{dt} = v_{\text{NO}_2} = k_2 [\text{O}_2] [\text{N}_2\text{O}_2]$$

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = v_{\text{N}_2\text{O}_2} = k_1 [\text{NO}]^2 - k_{-1} [\text{N}_2\text{O}_2] - k_2 [\text{O}_2] [\text{N}_2\text{O}_2]$$

According to the steady state approximation,

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = v_{\text{N}_2\text{O}_2} = k_1 [\text{NO}]^2 - k_{-1} [\text{N}_2\text{O}_2] - k_2 [\text{O}_2] [\text{N}_2\text{O}_2] = 0$$

$$k_1 [\text{NO}]^2 = k_{-1} [\text{N}_2\text{O}_2] + k_2 [\text{O}_2] [\text{N}_2\text{O}_2]$$

$$k_1 [\text{NO}]^2 = [\text{N}_2\text{O}_2] (k_{-1} + k_2 [\text{O}_2])$$

$$[\text{N}_2\text{O}_2] = \frac{k_1 [\text{NO}]^2}{(k_{-1} + k_2 [\text{O}_2])}$$

Substituting into the expression defining the rate of formation of  $[\text{NO}_2]$ ,

$$v_{\text{NO}_2} = k_2 [\text{O}_2][\text{N}_2\text{O}_2]$$
$$v_{\text{NO}_2} = k_2 [\text{O}_2] \left( \frac{k_1 [\text{NO}]^2}{(k_{-1} + k_2 [\text{O}_2])} \right)$$

$$v_{\text{NO}_2} = \frac{k_1 k_2 [\text{O}_2][\text{NO}]^2}{(k_{-1} + k_2 [\text{O}_2])}$$

In order for the rate equation reduce to second-order kinetics in NO and first-order kinetics in  $\text{O}_2$ ,  $k_{-1} \gg k_2$  so that we may eliminate a terms in the denominator. This yields the following:

$$v_{\text{NO}_2} = \frac{k_1 k_2 [\text{O}_2][\text{NO}]^2}{(k_{-1} + \cancel{k_2 [\text{O}_2]})}$$
$$v_{\text{NO}_2} = \frac{k_1 k_2}{k_{-1}} [\text{O}_2][\text{NO}]^2$$

Thus, the rate equation will be second-order kinetics in NO and first-order kinetics in  $\text{O}_2$  when,

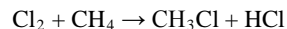
$$\boxed{k_{-1} \gg k_2}$$

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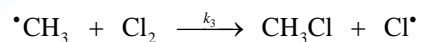
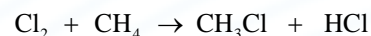
**\*10.9.** The gas-phase reaction:



proceeds by a free-radical chain reaction in which the chain propagators are Cl and  $\text{CH}_3$  (but not H), and the chain-ending step is  $2\text{Cl} \rightarrow \text{Cl}_2$ . Write the mechanism, identify the initiation reaction and the chain-propagating steps, and obtain an expression for the rate of the overall reaction.

**Solution:**

Following the method outlined in Section 10.5 Free Radical Reactions,



It is important to remember that the termination reaction always involves the regeneration of the initial species (the one that forms the free radicals in the first place).

We can apply the steady-state approximation for the chlorine and  $\text{CH}_3$  radicals in order to obtain an expression for the overall rate of reaction.

$$\frac{d[\text{Cl}^\bullet]}{dt} = \nu_{\text{Cl}^\bullet} = k_1[\text{Cl}_2] - k_2[\text{Cl}^\bullet][\text{CH}_4] + k_3[\text{Cl}_2][\text{CH}_3\text{Cl}] - k_{-1}[\text{Cl}^\bullet]^2$$

$$\frac{d[\bullet\text{CH}_3]}{dt} = \nu_{\bullet\text{CH}_3} = k_2[\text{Cl}^\bullet][\text{CH}_4] - k_3[\text{Cl}_2][\text{CH}_3\text{Cl}]$$

$$\frac{d[\text{HCl}]}{dt} = \nu_{\text{HCl}} = k_2[\text{Cl}^\bullet][\text{CH}_4]$$

$$\frac{d[\text{Cl}^\bullet]}{dt} = v_{\text{Cl}^\bullet} = k_1[\text{Cl}_2] - k_2[\text{Cl}^\bullet][\text{CH}_4] + k_3[\text{Cl}_2][\text{CH}_3\text{Cl}] - k_{-1}[\text{Cl}^\bullet]^2 = 0 \quad (1)$$

$$\frac{d[\text{CH}_3^\bullet]}{dt} = v_{\text{CH}_3^\bullet} = k_2[\text{Cl}^\bullet][\text{CH}_4] - k_3[\text{Cl}_2][\text{CH}_3\text{Cl}] = 0 \quad (2)$$

We recognize that the equations (1) and (2) have some common terms, such as  $k_2[\text{Cl}^\bullet][\text{CH}_4]$  and  $k_3[\text{Cl}_2][\text{CH}_3\text{Cl}]$ . Since both equations equal to 0, we can add them together in order those terms, and their sum still adds up to 0.

(1) + (2) :

$$k_1[\text{Cl}_2] - \cancel{k_2[\text{Cl}^\bullet][\text{CH}_4]} + \cancel{k_3[\text{Cl}_2][\text{CH}_3\text{Cl}]} - k_{-1}[\text{Cl}^\bullet]^2 + \cancel{k_2[\text{Cl}^\bullet][\text{CH}_4]} - \cancel{k_3[\text{Cl}_2][\text{CH}_3\text{Cl}]} = 0$$

$$k_1[\text{Cl}_2] - k_{-1}[\text{Cl}^\bullet]^2 = 0$$

$$[\text{Cl}^\bullet] = \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{Cl}_2]^{1/2}$$

Substituting into the rate equation for the formation of HCl,

$$v_{\text{HCl}} = k_2[\text{Cl}^\bullet][\text{CH}_4]$$

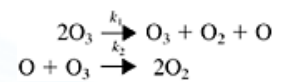
$$v_{\text{HCl}} = k_2 \left( \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{Cl}_2]^{1/2} \right) [\text{CH}_4]$$

$$v_{\text{HCl}} = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{CH}_4][\text{Cl}_2]^{1/2}$$

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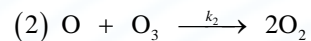
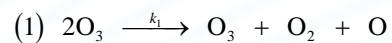
**10.10.** The following mechanism has been proposed for the thermal decomposition of pure ozone in the gas phase:



Derive the rate equation.

**Solution:**

Following the same method as we have done for the previous problems;



$$\frac{d[\text{O}_2]}{dt} = v_{\text{O}_2} = k_1 [\text{O}_3]^2 + k_2 [\text{O}][\text{O}_3]$$

$$\frac{d[\text{O}]}{dt} = v_{\text{O}} = k_1 [\text{O}_3]^2 - k_2 [\text{O}][\text{O}_3]$$

Applying the steady state approximation to O,

$$\frac{d[\text{O}]}{dt} = v_{\text{O}} = k_1 [\text{O}_3]^2 - k_2 [\text{O}][\text{O}_3] = 0$$

$$k_1 [\text{O}_3]^2 = k_2 [\text{O}][\text{O}_3]$$

$$[\text{O}] = \frac{k_1 [\text{O}_3]^2}{k_2 [\text{O}_3]}$$

$$[\text{O}] = \frac{k_1}{k_2} [\text{O}_3]$$

Substitution into the expression for the rate of formation of oxygen yields,

$$v_{\text{O}_2} = k_1 [\text{O}_3]^2 + k_2 [\text{O}] [\text{O}_3]$$

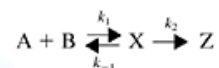
$$v_{\text{O}_2} = k_1 [\text{O}_3]^2 + \cancel{k_2} \left( \frac{k_1}{\cancel{k_2}} [\text{O}_3] \right) [\text{O}_3]$$

$$v_{\text{O}_2} = k_1 [\text{O}_3]^2 + k_1 [\text{O}_3]^2$$

$$\boxed{v_{\text{O}_2} = 2k_1 [\text{O}_3]^2}$$

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\*10.11. A reaction occurs by the mechanism:

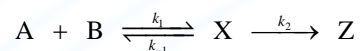


and the concentration of X is sufficiently small compared with the concentrations of A and B that the steady-state treatment applies. Prove that the activation energy  $E_a$  at any temperature is given by:

$$E_a = \frac{k_{-1}(E_1 + E_2 - E_{-1}) + k_2 E_1}{k_{-1} + k_2}$$

that is, is the weighted mean of the values  $E_1 + E_2 - E_{-1}$ , and  $E_1$ , which apply, respectively, to the limiting cases of  $k_1 \gg k_2$  and  $k_2 \gg k_{-1}$ .

**Solution:**



$$\frac{d[X]}{dt} = v_X = k_1[A][B] - k_{-1}[X] - k_2[X]$$

$$\frac{d[Z]}{dt} = v_Z = k_2[X]$$

Applying the steady state approximation to substance X,

$$\frac{d[X]}{dt} = v_X = k_1[A][B] - k_{-1}[X] - k_2[X] = 0$$

$$k_1[A][B] = k_{-1}[X] + k_2[X]$$

$$k_1[A][B] = [X](k_{-1} + k_2)$$

$$[X] = \frac{k_1[A][B]}{(k_{-1} + k_2)}$$

Substitution into the expression for the rate of formation of substance Z yields,

$$v_z = k_2 [X]$$

$$v_z = k_2 \left( \frac{k_1 [A][B]}{(k_{-1} + k_2)} \right)$$

$$v_z = \frac{k_1 k_2 [A][B]}{(k_{-1} + k_2)}$$

Let the rate constant  $K = \frac{k_1 k_2}{(k_{-1} + k_2)}$  and taking the natural log we obtain,

$$\ln K = \ln \left( \frac{k_1 k_2}{k_{-1} + k_2} \right)$$

$$\ln K = \ln k_1 + \ln k_2 - \ln(k_{-1} + k_2)$$

Differentiating both sides with respect to temperature leads to,

$$\frac{d \ln K}{dT} = \frac{\ln k_1}{dT} + \frac{1}{k_2} \frac{dk_2}{dT} - \frac{1}{k_{-1} + k_2} \frac{d(k_{-1} + k_2)}{dT}$$

$$\frac{d \ln K}{dT} = \frac{\ln k_1}{dT} + \frac{1}{k_2} \frac{dk_2}{dT} - \frac{1}{k_{-1} + k_2} \frac{dk_{-1}}{dT} - \frac{1}{k_{-1} + k_2} \frac{dk_2}{dT}$$

$$\frac{d \ln K}{dT} = \frac{\ln k_1}{dT} + \frac{dk_2}{dT} \left( \frac{1}{k_2} - \frac{1}{k_{-1} + k_2} \right) - \frac{k_{-1}}{k_{-1}(k_{-1} + k_2)} \frac{dk_{-1}}{dT}$$

$$\frac{d \ln K}{dT} = \frac{\ln k_1}{dT} + \frac{dk_2}{dT} \frac{k_{-1} + \cancel{k_2} - \cancel{k_2}}{k_2(k_{-1} + k_2)} - \frac{k_{-1}}{k_{-1} + k_2} \frac{\ln k_{-1}}{dT}$$

$$\frac{d \ln K}{dT} = \frac{\ln k_1}{dT} + \frac{k_{-1}}{k_{-1} + k_2} \frac{d \ln k_2}{dT} - \frac{k_{-1}}{k_{-1} + k_2} \frac{\ln k_{-1}}{dT}$$

Recall that Eq. 9.63 states,

$$\frac{\ln k_1}{dT} = C + \frac{E_1}{RT^2}$$

Rearranging to isolate the activation energy,

$$E_1 \equiv RT^2 \frac{\ln k_1}{dT} \text{ similarly, } E_{-1} \equiv RT^2 \frac{\ln k_{-1}}{dT} \text{ and } E_2 \equiv RT^2 \frac{\ln k_2}{dT}$$

Substituting these expressions into the differentiated expression above yields,

$$E = RT^2 \frac{d \ln K}{dT} \text{ and therefore,}$$

$$E = E_1 + \frac{k_{-1}}{k_{-1} + k_2} E_2 - \frac{k_{-1}}{k_{-1} + k_2} E_{-1}$$

We can combine the terms by putting them over a common denominator.

$$E = \frac{E_1(k_{-1} + k_2)}{k_{-1} + k_2} + \frac{E_2 k_{-1}}{k_{-1} + k_2} - \frac{E_{-1} k_{-1}}{k_{-1} + k_2}$$

$$E = \frac{E_1 k_{-1} + E_1 k_2 + E_2 k_{-1} - E_{-1} k_{-1}}{k_{-1} + k_2}$$

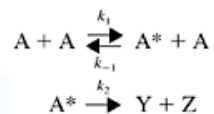
Further simplification leads to the desired equation,

$$E = \frac{E_1 k_2 + k_{-1} (E_1 + E_2 - E_{-1})}{k_{-1} + k_2}$$

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**10.12.** F. A. Lindemann [*Trans. Faraday Soc.*, 17, 598(1922)] proposed the following mechanism for a unimolecular gas reaction:



The species  $\text{A}^*$  is an energized molecule that is present in low concentrations. Apply the steady-state treatment to  $\text{A}^*$  and obtain an expression for the rate in terms of  $[\text{A}]$ ,  $k_1$ ,  $k_{-1}$ , and  $k_2$ . Show that the mechanism predicts first-order kinetics at higher  $\text{A}$  concentrations and second-order kinetics at lower ones.

**Solution:**

Given: see above

Required: expression for rate,  $k_1$ ,  $k_{-1}$ ,  $k_2$

$$\frac{d[\text{A}]}{dt} = v_{\text{A}} = k_1[\text{A}]^2 - k_{-1}[\text{A}][\text{A}^*]$$

$$\frac{d[\text{A}^*]}{dt} = v_{\text{A}^*} = k_1[\text{A}]^2 - k_{-1}[\text{A}][\text{A}^*] - k_2[\text{A}^*]$$

Applying the Steady-State treatment to  $\text{A}^*$  we obtain the following expression:

$$\frac{d[\text{A}^*]}{dt} = 0$$

$$v_{\text{A}^*} = k_1[\text{A}]^2 - k_{-1}[\text{A}][\text{A}^*] - k_2[\text{A}^*] = 0$$

Rearranging and simplifying we obtain,

$$k_1[\text{A}]^2 = k_{-1}[\text{A}][\text{A}^*] + k_2[\text{A}^*]$$

$$k_1[\text{A}]^2 = [\text{A}^*](k_{-1}[\text{A}] + k_2)$$

$$[\text{A}^*] = \frac{k_1[\text{A}]^2}{(k_{-1}[\text{A}] + k_2)}$$



The rate is given by,

$$v = k_2 [A^*]$$

We may substitute the above expression for  $A^*$  which yields,

$$v = \frac{k_1 k_2 [A]^2}{(k_{-1} [A] + k_2)}$$

At high pressures, we can work under the assumption that  $k_{-1} [A] \gg k_2$  therefore enabling us to remove the  $k_2$  term in the denominator and further simplify the expression.

$$v = \frac{k_1 k_2 [A]^2}{(k_{-1} [A] + \cancel{k_2})} \rightarrow \frac{k_1 k_2 [A]^2}{k_{-1} \cancel{[A]}} \quad (\text{a first order rate equation})$$

$$v = \frac{k_1 k_2}{k_{-1}} [A]$$

At low pressure, we can work under the assumption that  $k_2 \gg k_{-1} [A]$  and thus,

$$v = \frac{k_1 k_2 [A]^2}{(\cancel{k_{-1} [A]} + k_2)} \rightarrow \frac{k_1 \cancel{k_2} [A]^2}{\cancel{k_2}} \quad (\text{a second order rate equation})$$

$$v = k_1 [A]^2$$

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**\*10.13.** Certain polymerizations involve esterification reactions between  $\text{-COOH}$  groups on one molecule and  $\text{-OH}$  groups on another. Suppose that the concentration of such functional groups is  $c$  and that the rate of their removal by esterification obeys the equation:

$$-\frac{dc}{dt} = kc^2$$

Obtain an equation relating the time  $t$  to the fraction  $f$  of functional groups remaining and to the initial concentration  $c_0$  of functional groups.

**Solution:**

Given the differential equation  $-\frac{dc}{dt} = kc^2$ , we can start by choosing the boundary condition that at  $t = 0$ ,  $c = c_0$ . Rearranging the above expression and taking the integral of both sides, we obtain,

$$-\frac{dc}{c^2} = kdt$$

$$-\int \frac{dc}{c^2} = \int kdt$$

$$\frac{1}{c} = kt + I$$

Applying the boundary conditions to solve for  $I$ ,

$$\frac{1}{c} = \cancel{kt} + I$$

$$I = \frac{1}{c_0}$$

Substituting this back into the integrated expression,

$$\frac{1}{c} - \frac{1}{c_0} = kt$$

This can be rewritten as,

$$kt = \frac{c_0 - c}{cc_0}$$

The expression for the fraction of functional groups remaining is therefore,

$$f = \frac{c_0 - c}{c_0}$$

Let us derive an expression relation the fraction of functional groups remaining to the initial concentration only,

$$\frac{f}{1-f} = \frac{\frac{c_0 - c}{c_0}}{\frac{c_0 - c}{c_0} - \frac{c_0 - c}{c_0}} = \frac{\frac{c_0 - c}{c_0}}{\frac{c}{c_0}} = \frac{c_0 - c}{c} = c_0 kt$$

Inverting the above expression:

$$\frac{1-f}{f} = \frac{1}{c_0 kt}$$

$$\frac{1}{f} - 1 = \frac{1}{c_0 kt}$$

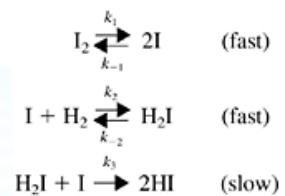
$$\frac{1}{f} = \frac{1}{c_0 kt} + 1 = \frac{1 + c_0 kt}{c_0 kt}$$

$$f = \frac{c_0 kt}{1 + c_0 kt}$$

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\*10.14. Show that the mechanism:



leads to the result that the rate equation for the overall reaction is  $v = k[\text{H}_2][\text{I}_2]$ .

**Solution:**

Recall that when reactions occur as fast equilibriums, we may write,

$$(1) \quad K = \frac{k_1}{k_{-1}} = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$(2) \quad K = \frac{k_2}{k_{-2}} = \frac{[\text{H}_2\text{I}]}{[\text{I}][\text{H}_2]}$$

Let us now rearrange these expressions in order to isolate I and  $\text{H}_2\text{I}$  as they are important reagents in the rate determining step. Finding expressions for these will allow us to determine the rate equation.

$$\frac{k_1}{k_{-1}} = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$[\text{I}]^2 = \frac{k_1}{k_{-1}} [\text{I}_2]$$

$$[\text{I}] = \left( \frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [\text{I}_2]^{\frac{1}{2}}$$

$$\frac{k_2}{k_{-2}} = \frac{[\text{H}_2\text{I}]}{[\text{I}][\text{H}_2]}$$

$$[\text{H}_2\text{I}] = \frac{k_2}{k_{-2}} [\text{I}][\text{H}_2]$$

Now substitute the expression for I into the above to obtain,

$$[\text{H}_2\text{I}] = \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [\text{I}_2]^{\frac{1}{2}} [\text{H}_2]$$

The overall rate is given by the rate determining step which is the slow reaction in this case.

$$\nu = k_3 [\text{H}_2\text{I}] [\text{I}]$$

Substitution yields,

$$\nu = k_3 \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [\text{I}_2]^{\frac{1}{2}} [\text{H}_2] \left( \frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [\text{I}_2]^{\frac{1}{2}}$$

Simplification yields,

$$\nu = k_3 \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [\text{I}_2]^{\frac{1}{2}} [\text{H}_2] \left( \frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [\text{I}_2]^{\frac{1}{2}}$$

$$\nu = \frac{k_3 k_2 k_1}{k_{-2} k_{-1}} [\text{I}_2] [\text{H}_2]$$

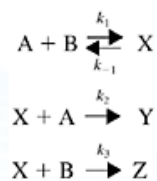
letting  $\frac{k_3 k_2 k_1}{k_{-2} k_{-1}} = k$ , we obtain the final expression for the rate equation

$$\boxed{\nu = k [\text{I}_2] [\text{H}_2]}$$

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**10.15.** Apply the steady-state treatment to the following mechanism, in which Y and Z are final products and X is a labile intermediate:



Obtain an expression for the rate of formation of the product Z. What rate equations are obtained if (a) A and (b) B are present in great excess?

**Solution:**

Given: see above

Required: expression for rate of formation of Z, a), b)

We will begin by writing out the rates of consumption or production for each of the reacting species involved. We *do* know, however, that X is the species for which we will be applying the steady-state treatment.

$$-\frac{d[\text{A}]}{dt} = v_{\text{A}} = k_1[\text{A}][\text{B}] - k_{-1}[\text{X}] + k_2[\text{A}][\text{X}]$$

$$-\frac{d[\text{B}]}{dt} = v_{\text{B}} = k_1[\text{A}][\text{B}] - k_{-1}[\text{X}] + k_3[\text{B}][\text{X}]$$

$$\frac{d[\text{X}]}{dt} = v_{\text{X}} = k_1[\text{A}][\text{B}] - k_{-1}[\text{X}] - k_2[\text{A}][\text{X}] - k_3[\text{B}][\text{X}]$$

Applying the steady-state treatment for X, we obtain,

$$\frac{d[\text{X}]}{dt} = 0$$

$$k_1[\text{A}][\text{B}] - k_{-1}[\text{X}] - k_2[\text{A}][\text{X}] - k_3[\text{B}][\text{X}] = 0$$

$$k_1[\text{A}][\text{B}] = k_{-1}[\text{X}] + k_2[\text{A}][\text{X}] + k_3[\text{B}][\text{X}]$$

This can be simplified by factoring out X from the right hand side.

$$k_1[A][B] = [X](k_{-1} + k_2[A] + k_3[B])$$

$$[X] = \frac{k_1[A][B]}{(k_{-1} + k_2[A] + k_3[B])}$$

Now we may write out the rates of formation for the product Z.

$$\frac{d[Z]}{dt} = v_Z = k_3[B][X]$$

Substituting what we have found (while applying the steady-state treatment to X) above into the expression for the rate of formation of Z we obtain,

$$v_Z = k_3[B][X]$$

$$v_Z = k_3[B] \frac{k_1[A][B]}{(k_{-1} + k_2[A] + k_3[B])}$$

$$v_Z = \frac{k_1 k_3 [A][B]^2}{(k_{-1} + k_2[A] + k_3[B])}$$

- a) If reagent A is present in great excess, then we can work under the assumption that  $k_2[A] \gg k_{-1} + k_3[B]$  which allows us to simplify the rate equation given above.

$$v_Z = \frac{k_1 k_3 [A][B]^2}{(\cancel{k_{-1}} + k_2[A] + \cancel{k_3[B]})}$$

$$v_Z = \frac{k_1 k_3 \cancel{[A]} [B]^2}{k_2 \cancel{[A]}} \quad (\text{a second order rate equation})$$

$$v_Z = \frac{k_1 k_3}{k_2} [B]^2$$

b) If the reagent B is present in great excess then we can work under the assumption  $k_3[B] \gg k_{-1} + k_2[A]$  thus,

$$v_z = \frac{k_1 k_3 [A][B]^2}{(\cancel{k_{-1}} + \cancel{k_2[A]} + k_3[B])}$$

$$v_z = \frac{k_1 \cancel{k_3} [A][B]^2}{\cancel{k_3[B]}} \quad (\text{a second order rate equation})$$

$$v_z = k_1 [A][B]$$

Since this simplified rate equation has the same form as that originally derived, the first reaction is rate determining.

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**10.16.** Calculate the maximum wavelength of the radiation that will bring about dissociation of a diatomic molecule having a dissociation energy of  $390.4 \text{ kJ mol}^{-1}$ .

**Solution:**

Given:  $E_{\text{diss}} = 390.4 \text{ kJ mol}^{-1}$

Required:  $\lambda_{\text{max}}$

We know that the dissociation energy given above is the total dissociation energy per mole. It is important to determine the dissociation energy in Joules. In order to do this, we will divide the dissociation energy by Avogadro's number.

$$E_{\text{diss}} = \frac{390.4 \text{ kJ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$E_{\text{diss}} = 6.482896 \times 10^{-22} \text{ kJ}$$

$$E_{\text{diss}} = 6.482896 \times 10^{-19} \text{ J}$$

With this energy, we can determine the corresponding frequency by using the following expression,

$$E = h\nu$$

$$\nu = \frac{E}{h}$$

Where  $h$  is Planck's constant and is measured in J s.

$$\nu = \frac{6.482896 \times 10^{-19} \cancel{\text{J}}}{6.626 \times 10^{-34} \cancel{\text{J}} \text{ s}}$$

$$\nu = 9.784027 \times 10^{14} \text{ s}^{-1}$$

The simple wave equation that relates the speed of light to wavelength and frequency can be used in order to determine the wavelength.

$$c = \lambda\nu$$

$$\lambda = \frac{c}{\nu}$$

Where  $c$  is the speed of light measured in  $\text{m s}^{-1}$ .

$$\lambda = \frac{2.998 \times 10^8 \text{ m } \cancel{\text{s}^{-1}}}{9.784\,027 \times 10^{14} \cancel{\text{s}^{-1}}}$$
$$\lambda = 3.06 \times 10^{-7} \text{ m}$$

Since wavelengths are typically expressed in terms on nanometers, we can write,

$$\lambda = 3.06 \times 10^{-7} \cancel{\text{m}} \left( \frac{1 \text{ nm}}{1 \times 10^{-9} \cancel{\text{m}}} \right)$$

$$\boxed{\lambda = 306 \text{ nm}}$$

This wavelength corresponds to the maximum wavelength that will cause dissociation of this diatomic molecule.

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**10.17.** Hydrogen iodide undergoes decomposition into  $\text{H}_2 + \text{I}_2$  when irradiated with radiation having a wavelength of 207 nm. It is found that when 1 J of energy is absorbed, 440  $\mu\text{g}$  of HI is decomposed. How many molecules of HI are decomposed by 1 photon of radiation of this wavelength? Suggest a mechanism that is consistent with this result.

**Solution:**

Given:  $\lambda = 207 \text{ nm}$ ,  $E = 1 \text{ J}$ ,  $m = 440 \mu\text{g}$

Required: number of molecules of HI decomposed

It is first important to determine the number of moles of HI in 440  $\mu\text{g}$ . We can do this by using the molar mass of HI.

$$n = \frac{m}{M}$$

$$440 \mu\text{g} = 440 \times 10^{-6} \text{ g}$$

$$n = \frac{440 \times 10^{-6} \cancel{\text{g}}}{127.9 \cancel{\text{g}} \text{ mol}^{-1}}$$

$$n = 3.440188 \times 10^{-6} \text{ mol}$$

With this, we are able to determine the number of molecules of HI by using Avogadro's number.

$$\# \text{ molecules} = 3.440188 \times 10^{-6} \cancel{\text{mol}} \left( 6.022 \times 10^{23} \cancel{\text{mol}^{-1}} \right)$$

$$\# \text{ molecules} = 2.071681 \times 10^{18}$$

Given the wavelength, we can determine the corresponding frequency as was done in the previous problem.

$$c = \lambda \nu$$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \cancel{\text{m}} \text{ s}^{-1}}{207 \times 10^{-9} \cancel{\text{m}}}$$

$$\nu = 1.448309 \times 10^{15} \text{ s}^{-1}$$

Using  $E = h\nu$ , we can determine the energy associated with this frequency and wavelength.

$$E = h\nu$$

$$E = (6.626 \times 10^{-34} \text{ J s}) (1.448\,309 \times 10^{15} \text{ s}^{-1})$$

$$E = 9.596\,497 \times 10^{-19} \text{ J}$$

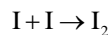
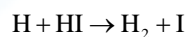
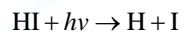
1 Joule of radiation will correspond to the following number of photons,

$$\# \text{ photons} = \frac{1 \text{ J}}{9.596\,497 \times 10^{-19} \text{ J}}$$

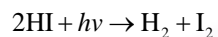
$$\# \text{ photons} = 1.04 \times 10^{18}$$

A single photon will then be able to decompose  $\frac{\# \text{ molecules}}{\# \text{ photons}} = \frac{2.071\,681 \times 10^{18}}{1.04 \times 10^{18}} = 1.99$ . Which is approximately 2 molecules of HI.

The German photochemist Emil Gabriel Warburg found for this reaction, a quantum yield of 2 (as we have just done). In order to explain this, he proposed the following mechanism:



When all three steps are added together, we obtain the following:



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**10.18.** A 100-watt mercury-vapor lamp emits radiation of 253.7 nm wavelength and may be assumed to operate with 100% efficiency. If all the light emitted is absorbed by a substance that is decomposed with a quantum yield of unity, how long will it take for 0.01 mol to be decomposed?

**Solution:**

Given:  $P = 100 \text{ W}$ ,  $\lambda = 253.7 \text{ nm}$ ,  $n = 0.01 \text{ mol}$

Required:  $t$  required to decompose

Let us first determine the frequency associated with the radiation of 253.7 nm.

$$c = \lambda \nu$$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{253.7 \times 10^{-9} \text{ m}}$$

$$\nu = 1.181\,711 \times 10^{15} \text{ s}^{-1}$$

The energy can be found using the following expression:

$$E = h\nu$$

$$E = (6.626 \times 10^{-34} \text{ J s}) (1.181\,711 \times 10^{15} \text{ s}^{-1})$$

$$E = 7.830 \times 10^{-19} \text{ J}$$

We know that a 100-W lamp emits 100 Joules per second (definition of a watt). Using this information, we can determine the number of photons emitted per second.

$$\# \text{ photons per second} = \frac{P}{E} = \frac{100 \text{ J s}^{-1}}{7.830 \times 10^{-19} \text{ J}}$$

$$\# \text{ photons per second} = 1.277\,137 \times 10^{20}$$

Since we are working in moles, let us change the above into molar units.

$$\frac{1.277\,137 \times 10^{20} \text{ s}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.120\,785 \times 10^{-4} \text{ moles of photons per second}$$

In order for 0.01 moles of this substance to be decomposed, it will require

$$t = \frac{0.01 \cancel{\text{mol}}}{2.120785 \times 10^{-4} \cancel{\text{mol}} \text{ s}^{-1}} = 47.15 \text{ s} = \boxed{47 \text{ s}}$$

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**10.19.** Suppose that the radiation emitted by the lamp in Problem 10.18 is all absorbed by ethylene, which decomposes into  $\text{C}_2\text{H}_2 + \text{H}_2$  with a quantum yield of unity. How much ethyne will be produced per hour?

**Solution:**

Given: Problem 10.18:  $P = 100 \text{ W}$ ,  $\lambda = 253.7 \text{ nm}$ ,  $n = 0.01 \text{ mol}$

Required: amount of ethylene produced per hour

The lamp in the previous problem was found to produce,

$$\frac{1.277 \times 10^{20} \text{ s}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.120785 \times 10^{-4} \text{ moles of photons per second}$$

Knowing this, we can determine how many moles of photons would be produced in 1 hour.

$$1 \text{ hour} = \frac{60 \text{ s}}{\text{min}} \times \frac{60 \text{ min}}{\text{hour}} = 3600 \text{ s}$$

$$n = 2.120785 \times 10^{-4} \text{ mol} \times \left( 3600 \frac{\cancel{\text{s}}}{\text{hour}} \right)$$

$$\boxed{n = 0.76 \frac{\text{mol}}{\text{hour}}}$$

Since ethylene is also a substance with a quantum yield of unity, then 0.76 moles of ethylene will be produced per hour.

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**10.20.** A 1000-watt mercury vapor flash lamp emits radiation of 253.7 nm wavelength, and the duration of the flash is 1  $\mu$ s. Suppose that all of the radiation of a single flash is absorbed by mercury vapor; how many atoms of excited mercury are formed?

**Solution:**

Given: flash lamp:  $P = 1000$  W,  $\lambda = 253.7$  nm,  $t = 1$   $\mu$ s

Required:  $N_{\text{Hg}}$  produced

We will begin by determining the frequency and energy associated with this wavelength.

$$c = \lambda \nu$$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{253.7 \times 10^{-9} \text{ m}}$$

$$\nu = 1.181\,711 \times 10^{15} \text{ s}^{-1}$$

$$E = h\nu$$

$$E = (6.626 \times 10^{-34} \text{ J s}) (1.181\,711 \times 10^{15} \text{ s}^{-1})$$

$$E = 7.830 \times 10^{-19} \text{ J}$$

Again, we know that a 1000-W lamp will emit 1000 Joules per second. With this, we can determine the number of photons emitted per second.

$$\# \text{ photons per second} = \frac{P}{E} = \frac{1000 \text{ J s}^{-1}}{7.830 \times 10^{-19} \text{ J}}$$

$$\# \text{ photons per second} = 1.277\,137 \times 10^{21}$$

In a single microsecond, which is equal to, 1  $\mu$ s =  $1 \times 10^{-6}$  s we will see that,

$$\# \text{ photons} = (1.277\,137 \times 10^{21} \text{ photons s}^{-1}) (1 \times 10^{-6} \text{ s})$$

$$\# \text{ photons} = 1.277 \times 10^{15} \text{ emitted}$$

Supposing that all of the radiation of a single flash (1 microsecond) is absorbed by mercury vapor, the number of photons emitted in this time will be equal to the number of excited mercury atoms formed.

$$N_{\text{Hg}} = 1.28 \times 10^{15} \text{ atoms}$$

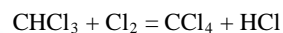
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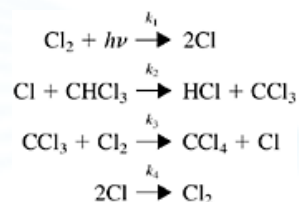
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**\*10.21.** The photochemical reaction between chlorine and chloroform in the gas phase follows the stoichiometric equation:



It is believed to occur by the mechanism:



Assume the rate of formation of Cl atoms in the initiation reaction to be  $2I_a$ , where  $I_a$  is the intensity of light absorbed, and obtain an expression for the overall rate in terms of  $I_a$  and  $[\text{CHCl}_3]$ .

**Solution:**

We will begin by writing down the steady-state expressions for Cl and  $\text{CCl}_3$ .

$$\frac{d[\text{Cl}]}{dt} = 2I_a - k_2[\text{Cl}][\text{CHCl}_3] + k_3[\text{CCl}_3][\text{Cl}_2] - k_4[\text{Cl}]^2$$

$$\frac{d[\text{Cl}]}{dt} = 0$$

$$2I_a - k_2[\text{Cl}][\text{CHCl}_3] + k_3[\text{CCl}_3][\text{Cl}_2] - k_4[\text{Cl}]^2 = 0$$

$$2I_a + k_3[\text{CCl}_3][\text{Cl}_2] = k_2[\text{Cl}][\text{CHCl}_3] + k_4[\text{Cl}]^2$$

$$\frac{d[\text{CCl}_3]}{dt} = k_2[\text{Cl}][\text{CHCl}_3] - k_3[\text{CCl}_3][\text{Cl}_2]$$

$$\frac{d[\text{CCl}_3]}{dt} = 0$$

$$k_2[\text{Cl}][\text{CHCl}_3] - k_3[\text{CCl}_3][\text{Cl}_2] = 0$$

$$k_2[\text{Cl}][\text{CHCl}_3] = k_3[\text{CCl}_3][\text{Cl}_2]$$

Adding the two steady-state expressions, we obtain the following:

$$2I_a - k_2[\text{Cl}][\text{CHCl}_3] + k_3[\text{CCl}_3][\text{Cl}_2] - k_4[\text{Cl}]^2 = 0$$

$$k_2[\text{Cl}][\text{CHCl}_3] - k_3[\text{CCl}_3][\text{Cl}_2] = 0$$

$$2I_a - k_4[\text{Cl}]^2 = 0$$

Solving for Cl,

$$2I_a = k_4[\text{Cl}]^2$$

$$[\text{Cl}]^2 = \frac{2I_a}{k_4}$$

$$[\text{Cl}] = \left( \frac{2I_a}{k_4} \right)^{\frac{1}{2}}$$

The overall rate equation is given by,

$$v = v_{\text{HCl}} = k_2[\text{Cl}][\text{CHCl}_3]$$

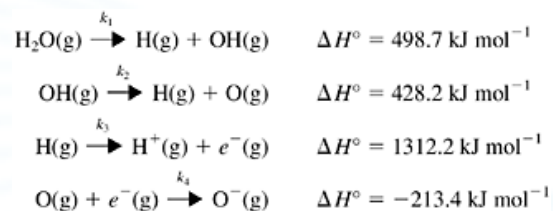
Substituting the expression for Cl into the above yields,

$$v = k_2 \left( \frac{2I_a}{k_4} \right)^{\frac{1}{2}} [\text{CHCl}_3]$$

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**\*10.22.** When water vapor is irradiated with a beam of high-energy electrons, various ions such as  $\text{H}^+$  and  $\text{O}^-$  appear. Calculate the minimum energies required for the formation of these ions, given the following thermochemical data:



Are the results you obtain consistent with the experimental appearance potentials of 19.5 eV for  $\text{H}^+$  and 7.5 eV for  $\text{O}^-$ ?

**Solution:**

Hydrogen ions are quite easily formed according to the following process:



This reaction can be generated through the addition of the following two equations:

- (1)  $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$
- (2)  $e^- + \text{H} \rightarrow \text{H}^+ + 2e^-$

The standard enthalpy of formation for the original reaction is therefore given by,

$$\Delta H^\circ = \Delta H^\circ(\text{rxn 1}) + \Delta H^\circ(\text{rxn 2})$$

$$\Delta H^\circ = (498.7 + 1312.2) \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = 1810.9 \text{ kJ mol}^{-1}$$

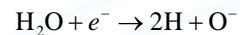
$$1 \text{ eV} = 96.47 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = 1810.9 \text{ kJ mol}^{-1} \times \frac{1 \text{ eV}}{96.47 \text{ kJ mol}^{-1}}$$

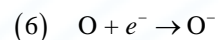
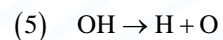
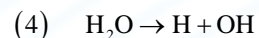
$$\boxed{\Delta H^\circ = 18.77 \text{ } 163 \text{ } 885 \text{ eV} \approx 18.8 \text{ eV}}$$

The above value is lower than the observed value of 19.5 eV, indicating that the system passes through a state of higher energy. The OH radical probably dissipates energy in the form of translational, vibrational, and rotational energy.

O<sup>-</sup> ions are most easily formed by



This reaction can be generated through the addition of the following three equations:



The standard enthalpy of formation for the original reaction is therefore given by,

$$\Delta H^\circ = \Delta H^\circ(\text{rxn 4}) + \Delta H^\circ(\text{rxn 5}) + \Delta H^\circ(\text{rxn 6})$$

$$\Delta H^\circ = (498.7 + 428.2 - 213.4) \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = 713.5 \text{ kJ mol}^{-1}$$

$$1 \text{ eV} = 96.47 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = 713.5 \text{ kJ mol}^{-1} \times \frac{1 \text{ eV}}{96.47 \text{ kJ mol}^{-1}}$$

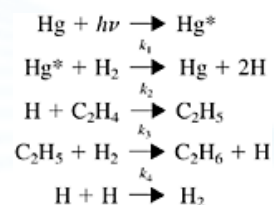
$$\boxed{\Delta H^\circ = 7.396\,081\,683 \text{ eV} \approx 7.4 \text{ eV}}$$

The above value is close to the observed appearance potential of 7.5 eV.

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**10.23.** The mercury-photosensitized hydrogenation of ethylene in the presence of mercury vapor is first-order with respect to ethylene and half-order with respect to  $H_2$ . Its rate is proportional to the square root of the intensity of the light absorbed. The following mechanism has been suggested to account for these observations:



Applying the steady-state approximation to  $[H]$  and  $[C_2H_5]$ , verify that the mechanism indeed supports the observations. What is the observed rate constant in terms of the rate constants of the elementary reactions?

**Solution:**

Applying the steady-state approximation for  $H$ , we obtain,

$$\frac{d[H]}{dt} = v_H = 2k_1[\text{Hg}^*][\text{H}_2] - k_2[H][\text{C}_2\text{H}_4] + k_3[\text{C}_2\text{H}_5][\text{H}_2] - k_4[H]^2$$

Applying the steady-state approximation to  $C_2H_5$ , we obtain,

$$\frac{d[C_2H_5]}{dt} = v_{C_2H_5} = k_2[H][\text{C}_2\text{H}_4] - k_3[C_2H_5][\text{H}_2]$$

Let us simplify both equations.

$$\frac{d[\text{H}]}{dt} = 0$$

$$2k_1[\text{Hg}^*][\text{H}_2] - k_2[\text{H}][\text{C}_2\text{H}_4] + k_3[\text{C}_2\text{H}_5][\text{H}_2] - k_4[\text{H}]^2 = 0$$

$$2k_1[\text{Hg}^*][\text{H}_2] + k_3[\text{C}_2\text{H}_5][\text{H}_2] = k_2[\text{H}][\text{C}_2\text{H}_4] + k_4[\text{H}]^2$$

$$\frac{d[\text{C}_2\text{H}_5]}{dt} = 0$$

$$k_2[\text{H}][\text{C}_2\text{H}_4] - k_3[\text{C}_2\text{H}_5][\text{H}_2] = 0$$

$$k_2[\text{H}][\text{C}_2\text{H}_4] = k_3[\text{C}_2\text{H}_5][\text{H}_2]$$

Adding both equations we obtain,

$$2k_1[\text{Hg}^*][\text{H}_2] + \cancel{k_3[\text{C}_2\text{H}_5][\text{H}_2]} = \cancel{k_2[\text{H}][\text{C}_2\text{H}_4]} + k_4[\text{H}]^2$$

$$\cancel{k_2[\text{H}][\text{C}_2\text{H}_4]} = \cancel{k_3[\text{C}_2\text{H}_5][\text{H}_2]}$$

$$2k_1[\text{Hg}^*][\text{H}_2] = k_4[\text{H}]^2$$

Isolating for H will yield,

$$2k_1[\text{Hg}^*][\text{H}_2] = k_4[\text{H}]^2$$

$$[\text{H}]^2 = \frac{2k_1[\text{Hg}^*][\text{H}_2]}{k_4}$$

$$[\text{H}] = \left( \frac{2k_1[\text{Hg}^*][\text{H}_2]}{k_4} \right)^{\frac{1}{2}}$$

Substituting this expression into the steady-state approximation for  $\text{C}_2\text{H}_5$ ,

$$\frac{d[\text{C}_2\text{H}_5]}{dt} = v_{\text{C}_2\text{H}_5} = k_2[\text{H}][\text{C}_2\text{H}_4] - k_3[\text{C}_2\text{H}_5][\text{H}_2] = 0$$

$$k_2[\text{H}][\text{C}_2\text{H}_4] = k_3[\text{C}_2\text{H}_5][\text{H}_2]$$

$$[\text{C}_2\text{H}_5] = \frac{k_2[\text{H}][\text{C}_2\text{H}_4]}{k_3[\text{H}_2]}$$

$$[\text{C}_2\text{H}_5] = \frac{k_2[\text{C}_2\text{H}_4]}{k_3[\text{H}_2]} \left( \frac{2k_1[\text{Hg}^*][\text{H}_2]}{k_4} \right)^{\frac{1}{2}}$$

The rate of formation of ethane is given by,

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = v_{\text{C}_2\text{H}_6} = k_3[\text{C}_2\text{H}_5][\text{H}_2]$$

This can also be written as,

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = v_{\text{C}_2\text{H}_6} = \cancel{k_3} \frac{k_2 \cancel{[\text{H}_2}][\text{C}_2\text{H}_4]}{\cancel{k_3} \cancel{[\text{H}_2]}} \left( \frac{2k_1[\text{Hg}^*][\text{H}_2]}{k_4} \right)^{\frac{1}{2}}$$

$$\boxed{\frac{d[\text{C}_2\text{H}_6]}{dt} = v_{\text{C}_2\text{H}_6} = k_2[\text{C}_2\text{H}_4] \left( \frac{2k_1[\text{Hg}^*][\text{H}_2]}{k_4} \right)^{\frac{1}{2}}}$$

The rate is indeed first order with respect to ethylene and half-order with respect to  $\text{Hg}^*$  and  $\text{H}_2$ . Since the number of moles of  $\text{Hg}^*$  produced is directly proportional to the intensity of the light absorbed, the rate is also proportional to the square root of the intensity of the light. The observed rate constant is therefore given by,

$$\boxed{k_{\text{obs}} = k_2 \left( \frac{2k_1}{k_4} \right)^{\frac{1}{2}}}$$

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**10.24.** The hydrolysis of a substance is specifically catalyzed by hydrogen ions, and the rate constant is given by:

$$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 4.7 \times 10^{-2} ([\text{H}^+]/\text{mol dm}^{-3})$$

When the substance was dissolved in a  $10^{-3} \text{ M}$  solution of an acid HA, the rate constant was  $3.2 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate the dissociation constant of HA.

**Solution:**

Given:  $k_0 = 4.7 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $C = 10^{-3} \text{ M}$ ,  $k_{\text{HA}} = 3.2 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Required:  $\alpha$

The concentration of  $\text{H}^+$  ions in the solution is:

$$\frac{3.2 \times 10^{-5}}{4.7 \times 10^{-2}} = 6.81 \times 10^{-4} \text{ mol dm}^{-3}$$

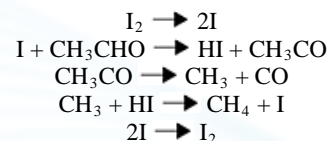
The dissociation constant is therefore

$$K_a = \frac{(6.81 \times 10^{-4})^2}{10^{-3}} = \boxed{4.64 \times 10^{-4} \text{ mol dm}^{-3}}$$

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**\*10.25.** The following is a slightly simplified version of the mechanism proposed in 1937 by G. K. Rollefson and R. F. Faull [*J. Amer. Chem. Soc.*, 59, 625(1937)] to explain the iodine-catalyzed decomposition of acetaldehyde:



Apply the steady-state treatment to I, CH<sub>3</sub>CO, and CH<sub>3</sub> and obtain an expression for the rate.

**Solution:**

We can first associate reaction constants to the above reactions as  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$ , and  $k_5$ . Then we can write out the rate of formation or consumption for the intermediate species I, CH<sub>3</sub>CO, and CH<sub>3</sub>. By the steady-state approximation, the rate of formation or consumption of these species equal to 0.

$$\frac{d[\text{I}]}{dt} = v_1 = 2k_1[\text{I}_2] - k_2[\text{I}][\text{CH}_3\text{CHO}] + k_4[\text{CH}_3][\text{HI}] - k_{-1}[\text{I}]^2$$

$$\frac{d[\text{I}]}{dt} = v_1 = 0$$

$$2k_1[\text{I}_2] - k_2[\text{I}][\text{CH}_3\text{CHO}] + k_4[\text{CH}_3][\text{HI}] - k_{-1}[\text{I}]^2 = 0$$

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = v_{\text{CH}_3\text{CO}} = k_2[\text{I}][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}]$$

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = v_{\text{CH}_3\text{CO}} = 0$$

$$k_2[\text{I}][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}] = 0$$

$$\frac{d[\text{CH}_3]}{dt} = v_{\text{CH}_3} = k_3[\text{CH}_3\text{CO}] - k_4[\text{CH}_3][\text{HI}]$$

$$\frac{d[\text{CH}_3]}{dt} = v_{\text{CH}_3} = 0$$

$$k_3[\text{CH}_3\text{CO}] - k_4[\text{CH}_3][\text{HI}] = 0$$

All three of these steady-state approximations can be added together in order to eliminate terms. This process yields the following result:

$$2k_1[I_2] - \cancel{k_2[I][CH_3CHO]} + \cancel{k_4[CH_3][HI]} - k_{-1}[I]^2 = 0$$

$$\cancel{k_2[I][CH_3CHO]} - \cancel{k_3[CH_3CO]} = 0$$

$$\cancel{k_3[CH_3CO]} - \cancel{k_4[CH_3][HI]} = 0$$

$$2k_1[I_2] - k_{-1}[I]^2 = 0$$

Rearrange and simplify to isolate I.

$$2k_1[I]^2 = k_{-1}[I_2]$$

$$[I]^2 = \frac{k_1}{2k_{-1}}[I_2]$$

$$[I] = \left( \frac{k_1}{2k_{-1}} \right)^{\frac{1}{2}} [I_2]^{\frac{1}{2}}$$

The overall rate is given by,

$$v_{\text{CO}} = k_3[CH_3CO] = k_2[I][CH_3CHO]$$

Making the substitution for I, we will get,

$$v_{\text{CO}} = k_2 \left( \frac{k_1}{2k_{-1}} \right)^{\frac{1}{2}} [I_2]^{\frac{1}{2}} [CH_3CHO]$$

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**\*10.26.** Suppose that a reaction is catalyzed by a series of homologous acids and that the Hammett equation (9.130) applies:

$$\log_{10} k_a = \log_{10} k_0 + \sigma \rho$$

where  $\sigma$  is the substituent constant and  $\rho$  is the reaction constant. Suppose that the corresponding equation for the dissociation of the acid is:

$$\log_{10} K_a = \log_{10} K_0 + \sigma \rho''$$

where  $\rho'$  is the reaction constant for the dissociation; the substituent constants are the same in both equations. Prove that the Brønsted equation:

$$k_a = G_a K_a^\alpha$$

applies. How does  $\alpha$  relate to the reaction constants  $\rho$  and  $\rho'$ ?

**Solution:**

The first two equations above may be written in the following manner:

$$\frac{1}{\rho} \log_{10} k_a = \frac{1}{\rho} \log_{10} k_0 + \sigma$$

$$\frac{1}{\rho''} \log_{10} K_a = \frac{1}{\rho''} \log_{10} K_0 + \sigma$$

Subtracting the second equation from the first yields,

$$\frac{1}{\rho} \log_{10} k_a - \frac{1}{\rho''} \log_{10} K_a = \text{constant}$$

Combine the terms to obtain,

$$\frac{1}{\rho} \log_{10} k_a - \frac{1}{\rho''} \log_{10} K_a = \text{constant}$$

$$\log_{10} k_a^{\frac{1}{\rho}} - \log_{10} K_a^{\frac{1}{\rho''}} = \text{constant}$$

$$\log_{10} \frac{k_a^{\frac{1}{\rho}}}{K_a^{\frac{1}{\rho''}}} = \text{constant}$$

This can also be written as,

$$\log_{10} \frac{k_a}{K_a^{\frac{\rho}{\rho''}}} = \text{constant}$$

Rearranging this expression to isolate  $k_a$ ,

$$\frac{k_a}{K_a^{\frac{\rho}{\rho''}}} = 10^{\text{constant}} = G$$

$$k_a = GK_a^{\frac{\rho}{\rho''}}$$

Note that  $\frac{\rho}{\rho''} = \alpha$  thus,

$$\boxed{k_a = GK_a^{\alpha}}$$

$\alpha$  represents the ratio of the two reaction constants.

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**10.27.** The hydrolysis of ethyl acetate catalyzed by hydrochloric acid obeys the rate equation:

$$v = k[\text{ester}][\text{HCl}]$$

and the reaction essentially goes to completion. At 25 °C the rate constant is  $2.80 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . What is the half-life of the reaction if  $[\text{ester}] = 0.1 \text{ M}$  and  $[\text{HCl}] = 0.01 \text{ M}$ ?

**Solution:**

Given:  $v = k[\text{ester}][\text{HCl}]$ ,  $T = 25 \text{ }^\circ\text{C}$ ,  $k = 2.80 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $[\text{ester}] = 0.1 \text{ M}$ ,

$$[\text{HCl}] = 0.01 \text{ M}$$

Required:  $t_{1/2}$

Since the reaction essentially goes to completion, we can assume that the concentration of hydrochloric acid remains unchanged throughout. We have also been given the rate equation which is first order with respect to HCl but is overall second order. We can use the concentration of HCl in order to determine the pseudo-first order rate constant.

Remembering that first order reactions have a rate constant with the units  $\text{s}^{-1}$  (Table 9.1),

$$k(2^{\text{nd}} \text{ order}) = 2.80 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$[\text{HCl}] = 0.01 \text{ M}$$

$1 \text{ M} = \text{mol L}^{-1}$ ,  $1 \text{ L} = 1 \text{ dm}^3$  therefore,

$$[\text{HCl}] = 0.01 \text{ M} = 0.01 \text{ mol dm}^{-3}$$

$$k' = k(2^{\text{nd}} \text{ order})[\text{HCl}]$$

$$k' = (2.80 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})(0.01 \text{ mol dm}^{-3})$$

$$k' = 2.80 \times 10^{-7} \text{ s}^{-1}$$

The half life for a first order reaction is given by Eq. 9.40:

$$t_{1/2} = \frac{\ln 2}{k}$$

This expression is also found in Table 9.1. Now, making the substitution of the pseudo-first order rate constant into Eq. 9.40 we obtain,

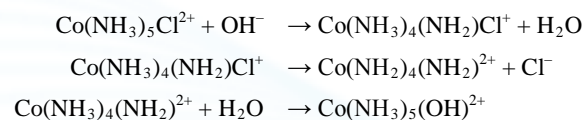
$$t_{1/2} = \frac{6.931\,472}{2.80 \times 10^{-7} \text{ s}^{-1}}$$

$$t_{1/2} = 2.48 \times 10^6 \text{ s}$$

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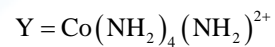
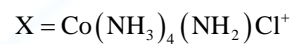
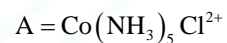
**10.28.** The following mechanism has been proposed for the alkaline hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ :



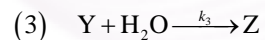
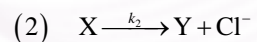
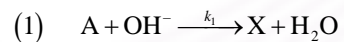
Assume  $\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}^+$  and  $\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+}$  to be in the steady state and derive an expression for the rate of reaction. Experimentally, the rate is proportional to  $[\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}] [\text{OH}^-]$ ; does this fact tell us anything about the relative magnitudes of the rate constants?

**Solution:**

Let's make a couple of substitutions in order to simplify the list of reactions.



Rewriting the above reaction sequence we obtain,



Applying the steady state approximation to substance X,



$$\frac{d[X]}{dt} = v_X = k_1[A][OH^-] - k_2[X]$$

$$\frac{d[X]}{dt} = v_X = 0$$

$$k_1[A][OH^-] = k_2[X]$$

$$[X] = \frac{k_1}{k_2}[A][OH^-]$$

Applying the steady state approximation to substance Y,

$$\frac{d[Y]}{dt} = v_Y = k_2[X] - k_3[Y][H_2O]$$

$$\frac{d[Y]}{dt} = v_Y = 0$$

$$k_2[X] = k_3[Y][H_2O]$$

$$[Y] = \frac{k_2}{k_3} \frac{[X]}{[H_2O]}$$

$$[Y] = \cancel{k_2} \left( \frac{k_1}{\cancel{k_2}} \frac{[A][OH^-]}{[H_2O]} \right)$$

$$[Y] = \frac{k_1}{k_3} \frac{[A][OH^-]}{[H_2O]}$$

The overall rate of reaction is therefore,

$$v_z = k_3[Y][H_2O]$$

$$v_z = \cancel{k_3} \frac{k_1 [A][OH^-]}{\cancel{k_3} [H_2O]} \cancel{[H_2O]}$$

$$v_z = k_1[A][OH^-]$$

$$v_z = k_1[Co(NH_3)_5Cl^{2+}][OH^-]$$

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**10.29.** Confirm that Eq. 10.68,

$$[\text{H}^+]_{\min} = (k_{\text{OH}^-} K_w / k_{\text{H}^+})^{\frac{1}{2}}$$

follows from Eq. 10.66,

$$k = k_0 + k_{\text{H}^+} [\text{H}^+] + \frac{k_{\text{OH}^-} K_w}{[\text{H}^+]}$$

**Solution:**

We have been told that,

$$k = k_0 + k_{\text{H}^+} [\text{H}^+] + \frac{k_{\text{OH}^-} K_w}{[\text{H}^+]}$$

This expression may be differentiated with respect to  $[\text{H}^+]$ . This process yields,

$$\frac{dk}{d[\text{H}^+]} = \frac{d}{d[\text{H}^+]} \left\{ k_0 + k_{\text{H}^+} [\text{H}^+] + \frac{k_{\text{OH}^-} K_w}{[\text{H}^+]} \right\}$$

$$\frac{dk}{d[\text{H}^+]} = k_{\text{H}^+} - \frac{k_{\text{OH}^-} K_w}{[\text{H}^+]^2}$$

Setting this expression equal to zero will allow us to further simplify and isolate for  $[\text{H}^+]_{\min}$ .

$$k_{\text{H}^+} - \frac{k_{\text{OH}^-} K_w}{[\text{H}^+]^2} = 0$$

$$k_{\text{H}^+} = \frac{k_{\text{OH}^-} K_w}{[\text{H}^+]^2}$$

$$[\text{H}^+]^2 = \frac{k_{\text{OH}^-} K_w}{k_{\text{H}^+}}$$

$$[\text{H}^+] = \left( \frac{k_{\text{OH}^-} K_w}{k_{\text{H}^+}} \right)^{\frac{1}{2}}$$

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**10.30.** The following results have been obtained by D. B. Dahlberg and F. A. Long [*J. Amer. Chem. Soc.*, 95, 3825(1973)] for the base-catalyzed enolization of 3-methyl acetone.

Catalyst	$\text{ClCH}_2\text{COO}^-$	$\text{CH}_3\text{COO}^-$	$\text{HPO}_4^{2-}$
$K_a/\text{mol dm}^{-3}$	$1.39 \times 10^{-3}$	$1.80 \times 10^{-5}$	$6.25 \times 10^{-8}$
$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$1.41 \times 10^{-3}$	$1.34 \times 10^{-2}$	0.26

Estimate the Brønsted coefficient  $\beta$ .

**Solution:**

Given: see above

Required: Brønsted coefficient  $\beta$

Recall that  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ . Since we have been given the acid dissociation constants and we require the base dissociation constants given by,

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \text{ and } K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]}$$

We can convert the acid dissociation constants into base dissociation constants by dividing  $10^{-14}$  by each value.

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{A}^-][\text{H}^+]} \rightarrow \cancel{[\text{H}^+]}[\text{OH}^-] \times \frac{[\text{HA}]}{[\text{A}^-]\cancel{[\text{H}^+]}}$$

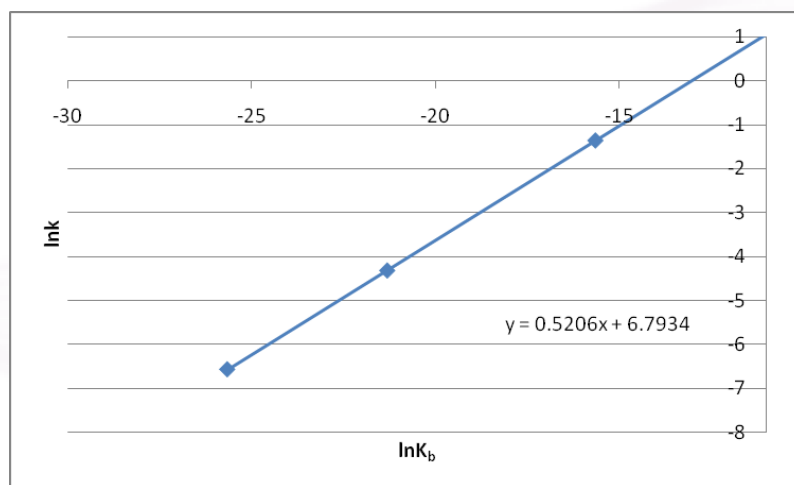
$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{A}^-][\text{H}^+]} \rightarrow \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

which can be expressed as:

$$\frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \rightarrow K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

We should also take the natural log of  $K_b$  and  $k$  in order to plot them against each other. By doing this, we will produce a straight-line graph whose slope is equal to the Brønsted coefficient.

Catalyst	$\text{ClCH}_2\text{COO}^-$	$\text{CH}_3\text{COO}^-$	$\text{HPO}_4^{2-}$
$K_b$	$7.19 \times 10^{-12}$	$5.56 \times 10^{-10}$	$1.60 \times 10^{-7}$
$k$	$1.41 \times 10^{-3}$	$1.34 \times 10^{-2}$	0.26
$\ln K_b$	-25.66	-21.31	-15.65
$\ln k$	-6.56	-4.31	-1.35



From the equation of the line generated by Microsoft Excel's trendline option, we can see that the slope of the curve is equal to,

$$m = 0.5206$$

$$m = \beta = 0.52$$

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**10.31.** Suggest a plausible mechanism for the bromination of acetone catalyzed by hydroxide ions. As with the acid-catalyzed reaction discussed in Section 10.9, the rate is independent of the bromine concentration.

**Solution:**

The hydroxide ion is assumed to abstract a proton from the acetone molecule, giving the ion  $\text{CH}_3\text{COCH}_2^-$ , which exists in a resonant state. If its resonance structure reacts rapidly with a bromine molecule, the rate is independent of the bromine concentration.

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**10.32.** It was found by J. Halpern and coworkers [*J. Phys. Chem.*, 60, 1455(1956)] that the rate equation for the oxidation of molecular hydrogen by dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) catalyzed by  $\text{Cu}^{2+}$  ions is of the form:

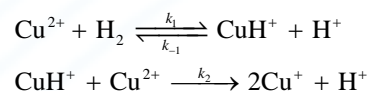
$$\nu = \frac{k[\text{H}_2][\text{Cu}^{2+}]^2}{[\text{H}_2] + k'[\text{Cu}^{2+}]}$$

(\*\*Note that the rate is independent of the concentration of dichromate ions.)

Suggest a mechanism consistent with this behavior, and apply the steady-state treatment to obtain the rate expression. Comment on rate-controlling steps corresponding to special cases of the mechanism.

**Solution:**

Since we know that the rate is independent of the concentration of dichromate ions, we will begin with the reaction that occurs between the hydrogen molecule and  $\text{Cu}^{2+}$ . This reaction can likely be said to reach equilibrium rapidly. The balanced reactions are as follows:



We can assume that the second step is the rate controlling step. Also, it should be noted that a third reaction (rapid) takes place with the dichromate ion. We will apply the steady state approximation for the  $\text{CuH}^+$  ion.

$$\frac{d[\text{CuH}^+]}{dt} = \nu_{\text{CuH}^+} = k_1[\text{Cu}^{2+}][\text{H}_2] - k_{-1}[\text{CuH}^+][\text{H}^+] - k_2[\text{CuH}^+][\text{Cu}^{2+}]$$

$$\frac{d[\text{CuH}^+]}{dt} = 0$$

$$k_1[\text{Cu}^{2+}][\text{H}_2] - k_{-1}[\text{CuH}^+][\text{H}^+] - k_2[\text{CuH}^+][\text{Cu}^{2+}] = 0$$

$$k_1[\text{Cu}^{2+}][\text{H}_2] = k_{-1}[\text{CuH}^+][\text{H}^+] + k_2[\text{CuH}^+][\text{Cu}^{2+}]$$

$$k_1[\text{Cu}^{2+}][\text{H}_2] = [\text{CuH}^+](k_{-1}[\text{H}^+] + k_2[\text{Cu}^{2+}])$$

$$[\text{CuH}^+] = \frac{k_1[\text{Cu}^{2+}][\text{H}_2]}{(k_{-1}[\text{H}^+] + k_2[\text{Cu}^{2+}])}$$



The overall rate can then be written as:

$$v_{2\text{Cu}^+} = k_2 [\text{CuH}^+][\text{Cu}^{2+}]$$

Making the appropriate substitutions into the above, we obtain,

$$v_{2\text{Cu}^+} = k_2 \frac{k_1 [\text{Cu}^{2+}][\text{H}_2]}{(k_{-1}[\text{H}^+] + k_2 [\text{Cu}^{2+}])} [\text{Cu}^{2+}]$$

This expression simplifies to the following:

$$v = \frac{k_1 k_2 [\text{H}_2][\text{Cu}^{2+}]^2}{(k_{-1}[\text{H}^+] + k_2 [\text{Cu}^{2+}])}$$

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**10.33.** For the oxidation of molecular hydrogen by dichromate ions catalyzed by  $\text{Ag}^+$  ions, A. H. Webster and J. Halpern [*J. Phys. Chem.*, 60, 280(1956)] obtained the rate equation:

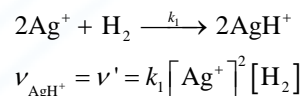
$$\nu = k[\text{H}_2][\text{Ag}^+]^2 + \frac{k'[\text{H}_2][\text{Ag}^+]^2}{[\text{H}_2] + k''[\text{Ag}^+]}$$

The existence of two terms suggests that two mechanisms are occurring in parallel. Suggest the two mechanisms, applying the steady-state treatment to obtain the second term in the rate equation.

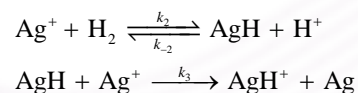
**Solution:**

In the previous problem, this particular reaction was catalyzed by copper ions (please refer back to it in order to review the reactions). However, here, we can see from the overall rate equation that there is an additional term (which means that two mechanisms are occurring in parallel).

It is safe to assume that the first term in the rate equation derives from a single step reaction involving a single hydrogen molecule and two  $\text{Ag}^+$  ions. Normally, we would not suggest that the order of each species is directly related to the stoichiometric values, but we will make this assumption in this particular case. We can write the reaction as follows:



This reaction can then be followed by the rapid reduction of the dichromate ion by the former product. Conversely, we can say that the  $\text{AgH}^+$  is rapidly oxidized by the dichromate ion. The next terms can be explained in the same way that the previous problem involving copper was.



Applying the steady-state approximation to reactions two and three we obtain,

$$\frac{d[\text{AgH}]}{dt} = v_{\text{AgH}} = k_2[\text{Ag}^+][\text{H}_2] - k_{-2}[\text{AgH}][\text{H}^+] - k_3[\text{AgH}][\text{Ag}^+]$$

$$\frac{d[\text{AgH}]}{dt} = 0$$

$$k_2[\text{Ag}^+][\text{H}_2] - k_{-2}[\text{AgH}][\text{H}^+] - k_3[\text{AgH}][\text{Ag}^+] = 0$$

$$k_2[\text{Ag}^+][\text{H}_2] = k_{-2}[\text{AgH}][\text{H}^+] + k_3[\text{AgH}][\text{Ag}^+]$$

$$k_2[\text{Ag}^+][\text{H}_2] = [\text{AgH}](k_{-2}[\text{H}^+] + k_3[\text{Ag}^+])$$

$$[\text{AgH}] = \frac{k_2[\text{Ag}^+][\text{H}_2]}{(k_{-2}[\text{H}^+] + k_3[\text{Ag}^+])}$$

The 'overall' rate equation can then be written as:

$$v_{\text{AgH}^+} = k_3[\text{AgH}][\text{Ag}^+]$$

Making the substitution for the AgH molecule into the expression above, we obtain,

$$v_{\text{AgH}^+} = k_3 \frac{k_2[\text{Ag}^+][\text{H}_2]}{(k_{-2}[\text{H}^+] + k_3[\text{Ag}^+])} [\text{Ag}^+]$$

This can be re-written as:

$$v'' = \frac{k_2 k_3 [\text{Ag}^+]^2 [\text{H}_2]}{(k_{-2}[\text{H}^+] + k_3[\text{Ag}^+])}$$

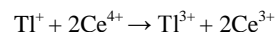
Putting both rate equations together, we will obtain the true rate equation.

$$\nu = \nu' + \nu''$$

$$\nu = 2k_1[\text{H}_2][\text{Ag}^+]^2 + \frac{k_2k_3[\text{H}_2][\text{Ag}^+]^2}{(k_{-2}[\text{H}^+] + k_3[\text{Ag}^+])}$$

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**10.34.** The reaction:



is catalyzed by  $\text{Ag}^+$  ions. Under certain conditions the rate is proportional to

$$[\text{Ce}^{4+}][\text{Tl}^+][\text{Ag}^+]/[\text{Ce}^{3+}]$$

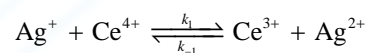
Suggest a mechanism consistent with this behavior.

**Solution:**

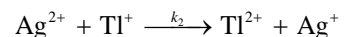
We are given that,

$$r \propto \frac{[\text{Ce}^{4+}][\text{Tl}^+][\text{Ag}^+]}{[\text{Ce}^{3+}]} \quad \text{and} \quad \text{Tl}^+ + 2\text{Ce}^{4+} \rightarrow \text{Tl}^{3+} + 2\text{Ce}^{3+}$$

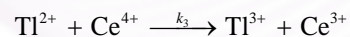
Since the overall rate equation consists of a ratio, we know that there must be more than a single reaction taking place. We can also guess that the first reaction is a rapid equilibrium and the second reaction is the rate controlling step (slow). We are also told that there is a catalyst involved so this will take part in the initial fast equilibrium reaction.



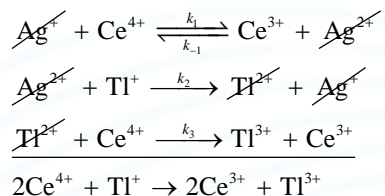
The newly oxidized silver ion will then react with  $\text{Tl}^+$  through an oxidation/reduction.



Since we know that the silver can only stably return to the +1 oxidation state via oxidation/reduction, we know that there must be a third step that involves  $\text{Tl}^{2+}$  in order to bring it to the fully oxidized form of +3. This next reaction will occur fairly quickly. From the first step, we can use the remaining  $\text{Ce}^{4+}$  as an oxidizing agent (which will in turn be reduced to  $\text{Ce}^{3+}$ ).



Let us verify our assumptions by adding up all of the reactions and checking to see whether all of the reactants and products are satisfied.



Recall that:

$$K = \frac{k_1}{k_{-1}} = \frac{[\text{Ag}^{2+}][\text{Ce}^{3+}]}{[\text{Ag}^+][\text{Ce}^{4+}]}$$

The overall rate of the reaction will be defined by the limiting step and is therefore;

$$\nu = k_2 [\text{Ag}^{2+}][\text{Ti}^+]$$

Making the appropriate rearrangements and simplifications to eliminate  $\text{Ag}^{2+}$  (by substitution from the equilibrium constant expression) we obtain,

$$\nu = k_2 \frac{K [\text{Ag}^+][\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} [\text{Ti}^+]$$

This can be re-written in as,

$$\nu = \frac{k_1 k_2}{k_{-1}} \frac{[\text{Ag}^+][\text{Ce}^{4+}][\text{Ti}^+]}{[\text{Ce}^{3+}]}$$

Thus proving that,

$$\nu \propto \frac{[\text{Ce}^{4+}][\text{Ti}^+][\text{Ag}^+]}{[\text{Ce}^{3+}]}$$

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**10.35.** The following rates have been obtained for an enzyme-catalyzed reaction at various substrate concentrations:

$10^3[\text{S}]/\text{mol dm}^{-3}$	Rate, $v$ /(arbitrary units)
0.4	2.41
0.6	3.33
1.0	4.78
1.5	6.17
2.0	7.41
3.0	8.70
4.0	9.52
5.0	10.5
10.0	12.5

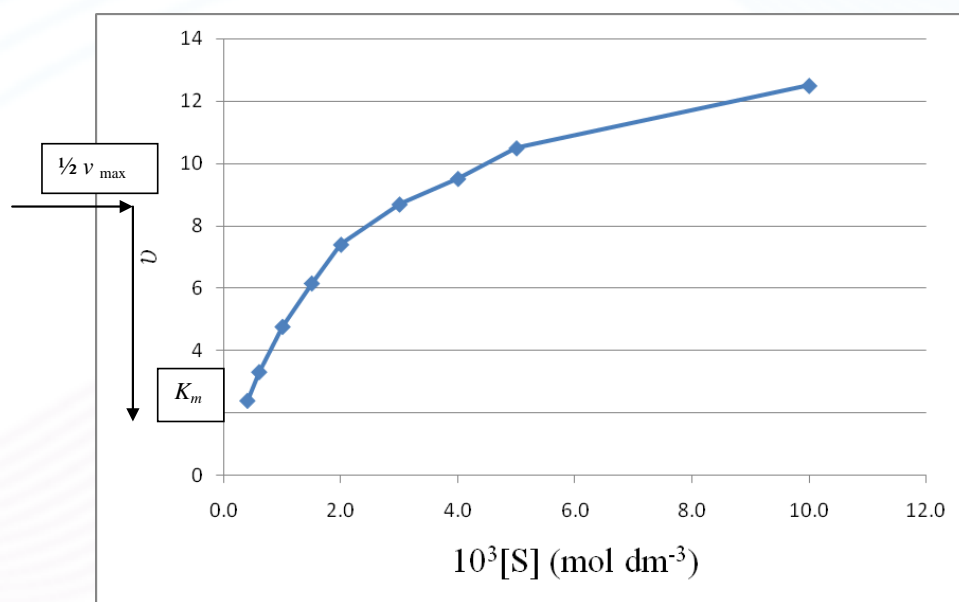
Plot  $v$  against  $[\text{S}]$ ,  $1/v$  against  $1/[\text{S}]$ , and  $v/[\text{S}]$  against  $v$ , and from each plot estimate the Michaelis constant. Which plot appears to give the most reliable value?

**Solution:**

In order to create all of these plots, let us first write out a table that includes all of the values that we will be required to use.

$10^3[\text{S}] (\text{mol dm}^{-3})$	$v$	$1/v$	$1/[\text{S}] (10^{-3} \text{ mol dm}^{-3})$	$v/[\text{S}] (10^{-3} \text{ mol dm}^{-3})$
0.4	2.41	0.4149	2.500	6.025
0.6	3.33	0.3003	1.667	5.550
1.0	4.78	0.2092	1.000	4.780
1.5	6.17	0.1621	0.667	4.113
2.0	7.41	0.1350	0.500	3.705
3.0	8.7	0.1149	0.333	2.900

4.0	9.52	0.1050	0.250	2.380
5.0	10.5	0.0952	0.200	2.100
10.0	12.5	0.0800	0.100	1.250

Plot 1:  $v$  against  $[S]$ 

The Michaelis-Menten equation (Eq. 10.82) states that,



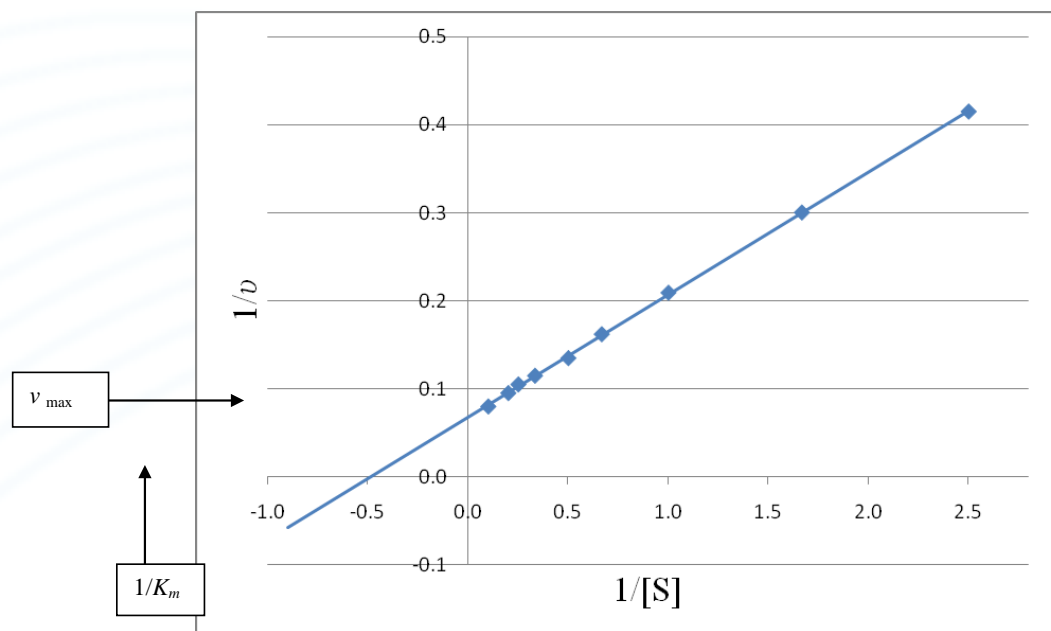
$$v = \frac{v_{\max} [S]}{K_m + [S]}$$

In this expression,  $K_m$  = Michaelis–Menten rate constant,  $[S]$  = substrate concentration,  $v$  = initial rate of production of the product, and  $v_{\max}$  = maximum initial rate of production of the product.

Notice that this plot produces a curved line which is not easy to work with. It essentially produces a saturation curve which is mostly only useful to examine the relationship between the concentration of substrate and the rate of reaction. Here, we would need to look at the steepest part of the slope which we can call a ‘straight line’. The highest point of this ‘straight line’ would be equal to  $\frac{1}{2} v_{\max}$ . From this point ( $\frac{1}{2} v_{\max}$ ), we could then draw a straight line down to the  $x$ -axis. This gives us the value of the Michaelis-Menten rate constant,  $K_m$ .

As you can guess, this particular method is not going to provide the most accurate or precise results due to the fact that there is a lot of guesswork and estimation involved. From the plot above, we have determined that  $K_m \approx 2 \times 10^{-3} \text{ mol dm}^{-3}$ .

Plot 2:  $1/v$  against  $1/[S]$



The Michaelis-Menten equation (Eq. 10.82) states that,

$$v = \frac{v_{\max} [S]}{K_m + [S]}$$

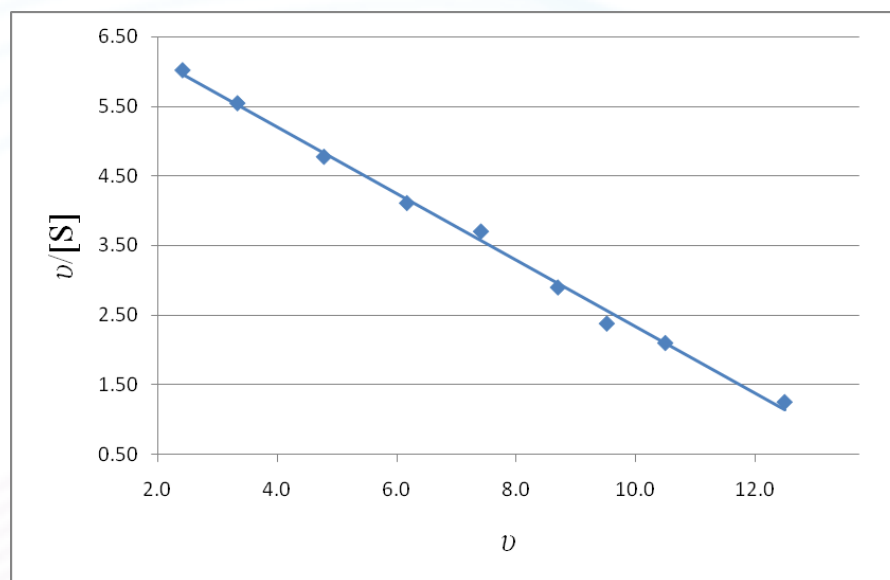
In this expression,  $K_m$  = Michaelis-Menten rate constant,  $[S]$  = substrate concentration,  $v$  = initial rate of production of the product, and  $v_{\max}$  = maximum initial rate of production of the product.

The type of plot that you see here is called a double reciprocal plot. It is quite often used in enzyme kinetics and therefore the student should become acquainted with this type of curve. Double reciprocal plots give us two pieces of critical information,  $v_{\max}$  and  $1/K_m$ . They give us this information in terms of y and x-intercept respectively. They can therefore be determined quite reliably (especially when using graphing programs). It is also interesting to examine plots for enzyme inhibition at a variety of concentrations in order to see the effects on  $v_{\max}$  and  $1/K_m$  (usually as the concentration increases). Double reciprocal plots also –by their shape– allow us to determine the type of enzyme inhibition/catalysis occurring in our experiment.

This plot has told us that,  $1/K_m = -0.5$  therefore,

$$K_m = |-0.5|^{-1} \rightarrow K_m = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

Plot 3:  $v/[S]$  against  $v$



The Michaelis-Menten equation (Eq. 10.82) states that,

$$v = \frac{v_{\max} [S]}{K_m + [S]}$$

In this expression,  $K_m$  = Michaelis-Menten rate constant,  $[S]$  = substrate concentration,  $v$  = initial rate of production of the product, and  $v_{\max}$  = maximum initial rate of production of the product.

The final plot above produces a beautiful straight line graph which will allow us to perform a linear regression and obtain the *exact* value for the Michaelis-Menten rate constant. Since we have plotted  $v/[S]$  against  $v$ , we can use the Michaelis-Menten equation to help us determine what we need to be looking for on the plot to give us our  $K_m$  value. It turns out that the slope of this plot allows us to determine  $K_m$ .

Upon performing a linear regression (using Microsoft Excel's linest function) we obtain the following regression statistics:

Linear Regression Statistics			
<b>m</b>	-0.479	7.123	<b>b</b>
<b>Sm</b>	0.011	0.087	<b>Sb</b>
<b>R<sup>2</sup></b>	0.996	0.104	<b>Sy</b>
<b>F</b>	1924.562	7	<b>DF</b>

The numerical value in the first row and column provides the exact value of the slope (for the third curve). Therefore,

$$1/K_m = -0.479$$

$$K_m = |-0.479|^{-1}$$

$$K_m = 2.09 \times 10^{-3} \text{ mol dm}^{-3}$$

So what is the difference between the second and third curves? As can be seen, the second plot is highly sensitive to increasingly large values of  $[S]$  because there is 'bunching' and crowding of the data points in that range. Looking at the far right of the plot, we can see that the double reciprocal method is less sensitive to small values of  $[S]$  and therefore does not produce an evenly populated curve.

The third curve is actually the best since it is both evenly populated and allows for proper statistical analysis such as a linear regression. Using the linear regression method, it is possible to determine (more precisely and accurately) the value for the Michaelis-Menten rate constant. It is the preferred method when working quantitatively in enzyme catalysis.

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**10.36.** The following data have been obtained for the myosin-catalyzed hydrolysis of ATP, at 25 °C and pH 7.0.

$10^5[\text{ATP}]/\text{mol dm}^{-3}$	$10^6v/\text{mol dm}^{-3} \text{ s}^{-1}$
7.5	0.067
12.5	0.095
20.0	0.119
32.5	0.149
62.5	0.185
155.0	0.191
320.0	0.195

Plot  $v$  against  $[\text{S}]$ ,  $1/v$  against  $1/[\text{S}]$ , and  $v/[\text{S}]$  against  $v$ , and from each plot calculate the Michaelis constant  $K_m$  and the limiting rate  $V$ .

**Solution:**

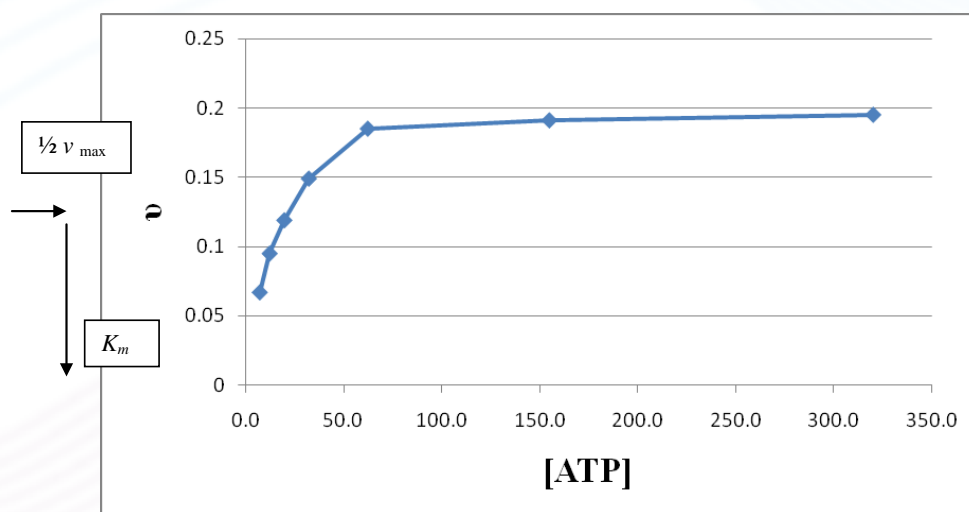
We will use the same method in this problem as we did in the previous.

$10^5[\text{ATP}]/\text{mol dm}^{-3}$	$10^6v/\text{mol dm}^{-3} \text{ s}^{-1}$	$1/v$	$1/[\text{S}]$	$v/[\text{S}]$
7.5	0.067	14.925	0.133	8.933E-03
12.5	0.095	10.526	0.080	7.600E-03
20.0	0.119	8.403	0.050	5.950E-03
32.5	0.149	6.711	0.031	4.585E-03
62.5	0.185	5.405	0.016	2.960E-03
155.0	0.191	5.236	0.006	1.232E-03

320.0	0.195	5.128	0.003	6.094E-04
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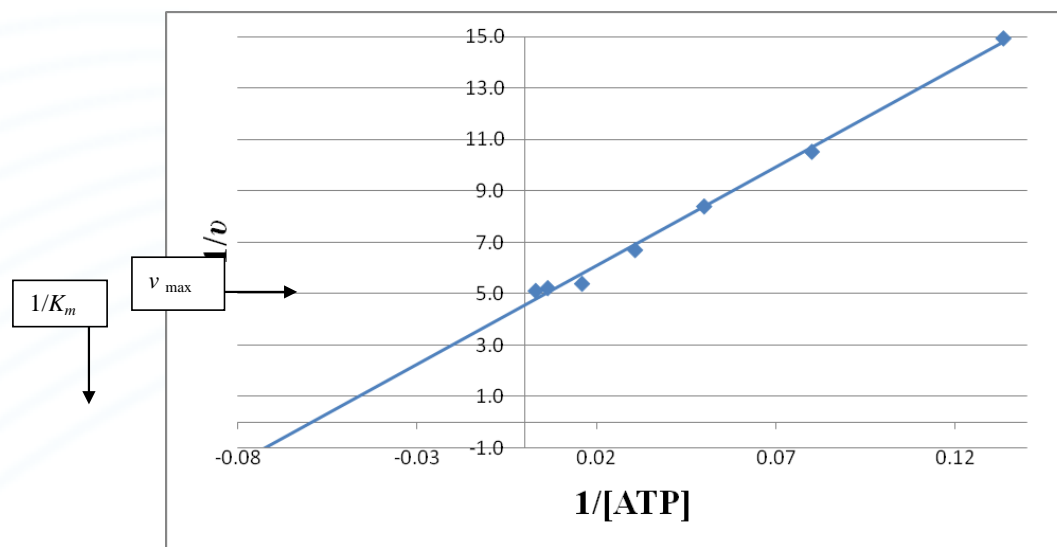
Note that the 'limiting rate' here is actually  $v_{\max}$  in plots two and three and is better described as twice the value at which saturation occurs in the first plot.

Plot 1:  $v$  against [ATP]



$$K_m \approx 16.7 \times 10^{-5} \text{ mol dm}^{-3} \text{ and } v_{\max} \approx 0.22 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$$

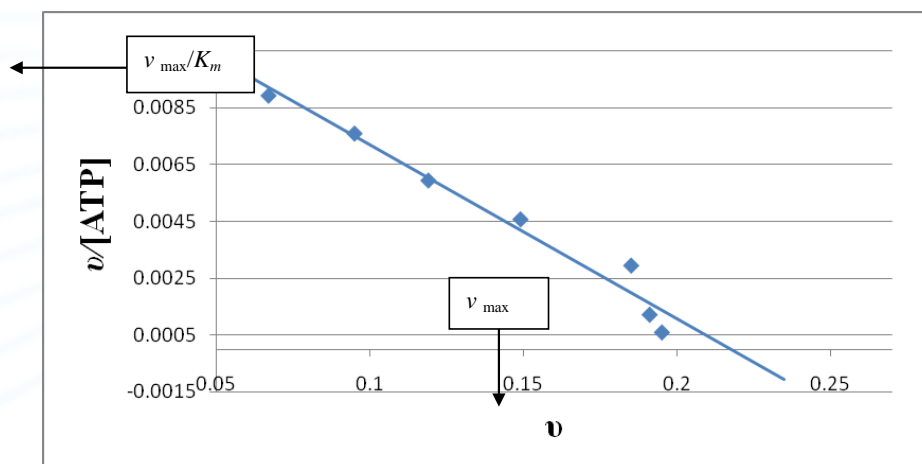
Plot 2:  $1/v$  against  $1/[ATP]$



$$1/K_m = -0.06 \rightarrow K_m = |-0.06|^{-1} \rightarrow K_m = 16.67 \times 10^{-5} \text{ mol dm}^{-3}$$

$$1/v_{\max} = 4.7 \rightarrow v_{\max} = 1/4.7 \rightarrow v_{\max} \approx 0.21 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Plot 3:  $v/[ATP]$  against  $v$



Linear regression statistics:

Linear Regression Statistics			
<b>m</b>	-0.061	0.013	<b>b</b>
<b>Sm</b>	0.005	0.001	<b>Sb</b>
<b>R<sup>2</sup></b>	0.968	0.001	<b>Sy</b>
<b>F</b>	149.196	5	<b>DF</b>

The numerical value located in the first row and column provides us with the value for the slope. As we have previously seen, the slope is equal to  $1/K_m$  therefore,

$$1/K_m = -0.061$$

$$K_m = |-0.061|^{-1}$$

$$K_m = 16.39 \times 10^{-5} \text{ mol dm}^{-3}$$



From the plot above, we can see that,

$$v_{\max} = 0.22 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$$

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**\*10.37.** The following values of  $V$  (limiting rate at high substrate concentrations) and  $K_m$  have been obtained at various temperatures for the hydrolysis of acetylcholine bromide, catalyzed by acetylcholinesterase.

$T/^{\circ}\text{C}$	$10^6 V / \text{mol dm}^{-3} \text{ s}^{-1}$	$K_m \times 10^4 / \text{mol dm}^{-3}$
20.0	1.84	4.03
25.0	1.93	3.75
30.0	2.04	3.35
35.0	2.17	3.05

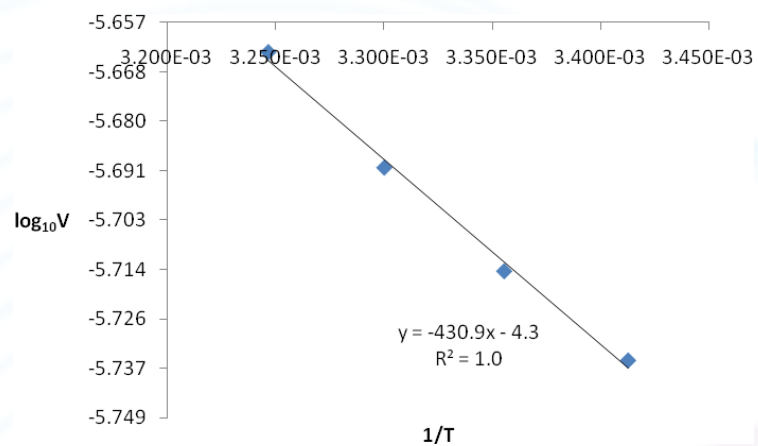
- a. Assuming the enzyme concentration to be  $1.00 \times 10^{-11} \text{ mol dm}^{-3}$ , calculate the energy of activation, the enthalpy of activation, the Gibbs energy of activation, and the entropy of activation for the breakdown of the enzyme-substrate complex at  $25^{\circ}\text{C}$ .
- b. Assuming  $K_m$  to be the dissociation constant  $k_{-1}/k_1$  for the enzyme-substrate complex ( $\text{ES} \xrightleftharpoons[k_1]{k_{-1}} \text{E} + \text{S}$ ), determine the following thermodynamic quantities for the *formation* of the enzyme-substrate complex at  $25^{\circ}\text{C}$ :  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ .
- c. From the results obtained in parts (a) and (b), sketch a Gibbs energy diagram and an enthalpy diagram for the reaction.

**Solution:**

Remember that we should change the temperature units to Kelvin! We will now construct a table that includes all of the values that we will need to generate the desired plots.

$T (\text{K})$	$V (\text{mol dm}^{-3} \text{ s}^{-1})$	$K_m (\text{mol dm}^{-3})$	$1/T (\text{K})$	$\text{Log}_{10}(V) (\text{mol dm}^{-3} \text{ s}^{-1})$	$\text{Log}_{10}(K_m) (\text{mol dm}^{-3})$
293	1.84E-06	4.03E-04	3.413E-03	-5.735	-3.395
298	1.93E-06	3.75E-04	3.356E-03	-5.714	-3.426
303	2.04E-06	3.35E-04	3.300E-03	-5.690	-3.475
308	2.17E-06	3.05E-04	3.247E-03	-5.664	-3.516

a) Slope of plot of  $\log_{10} V$  against  $1/T = -430.9\text{K}$



$$E = \ln 10 \times R \times \text{slope}$$

$$E = 19.14 \times 430.9 = 8247.426 \text{ J mol}^{-1}$$

$$\boxed{E = 8.25 \text{ kJ mol}^{-1}}$$

$$RT \text{ at } 25^\circ\text{C} = 8.314 \times 298 = 2478 \text{ J mol}^{-1} = 2.48 \text{ kJ mol}^{-1}$$

$$\Delta^\ddagger H = E - RT$$

$$\Delta^\ddagger H = 8.25 - 2.48$$

$$\boxed{\Delta^\ddagger H = 5.77 \text{ kJ mol}^{-1}}$$

$$\Delta^\ddagger G = 19.14 \times 7.51 \times 298.15$$

$$\Delta^\ddagger G = 42\,864.76\,623 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger G = 42.9 \text{ kJ mol}^{-1}}$$

$$\Delta^\ddagger S = \frac{5700 - 42\,856}{298.15}$$

$$\boxed{\Delta^\ddagger S = -124 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\text{At } 25.0^\circ\text{C}, V = 1.93 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$[E]_0 = 1.0 \times 10^{-11} \text{ mol dm}^3$$

$$k_c = V / [E]_0 = 1.93 \times 10^5 \text{ s}^{-1}$$

$$k_c = \frac{k_B T}{h} \exp(-\Delta^\ddagger G / RT); \frac{k_B T}{h} \text{ at } 25.0^\circ\text{C} = \frac{1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \times 298 \text{ K}}{6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}} = 6.21 \times 10^{12} \text{ s}^{-1}$$

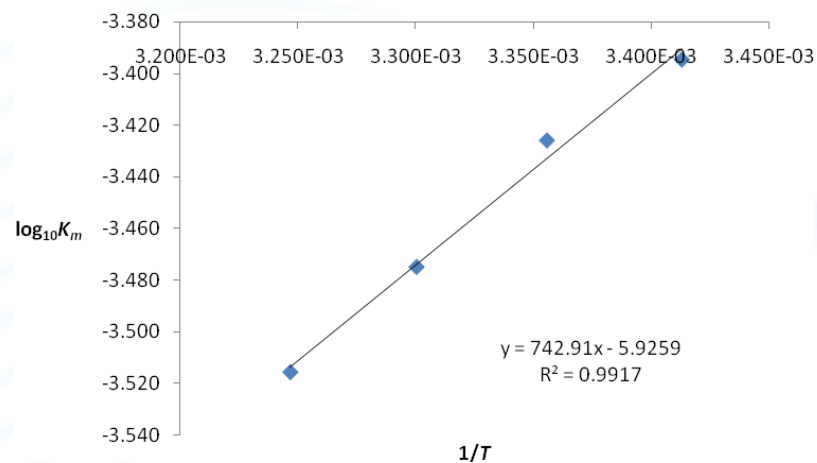
$$\exp(-\Delta^\ddagger G / RT) = k_c \frac{h}{k_B T} = \frac{1.93 \times 10^5 \text{ s}^{-1}}{6.21 \times 10^{12} \text{ s}^{-1}} = 3.108 \times 10^{-8} = 10^{-7.51}$$

$$\Delta^\ddagger G = -\ln(\exp(-\Delta^\ddagger G / RT)) \times RT$$

$$\Delta^\ddagger G = -\ln(10^{-7.51}) \times 8.314 \times 298.15$$

$$\Delta^\ddagger G = -\ln(10) \times (-7.51) \times 8.314 \times 298.15$$

b) Slope of  $\log_{10} K_m$  against  $1/T$  plot = 742.91



$$\Delta H^\circ \text{ (for dissociation)} = \ln 10 \times R \times \text{slope}$$

$$\Delta H^\circ \text{ (for dissociation)} = 19.14 \times 742.91$$

$$\Delta H^\circ \text{ (for dissociation)} = -14\,219.2974 \text{ J mol}^{-1}$$

$$\Delta H^\circ \text{ (for dissociation)} = -14.2 \text{ kJ mol}^{-1}$$

$$\text{At } 25.0^\circ\text{C}, \log_{10}(K_m) = -3.426$$

$$\Delta G^\circ \text{ (for dissociation)} = -\ln(K_m) \times RT$$

$$\Delta G^\circ \text{ (for dissociation)} = 19.14 \times 298.15 \times 3.426$$

$$\Delta G^\circ \text{ (for dissociation)} = 19\,550.78\,077 \text{ J mol}^{-1}$$

For association,

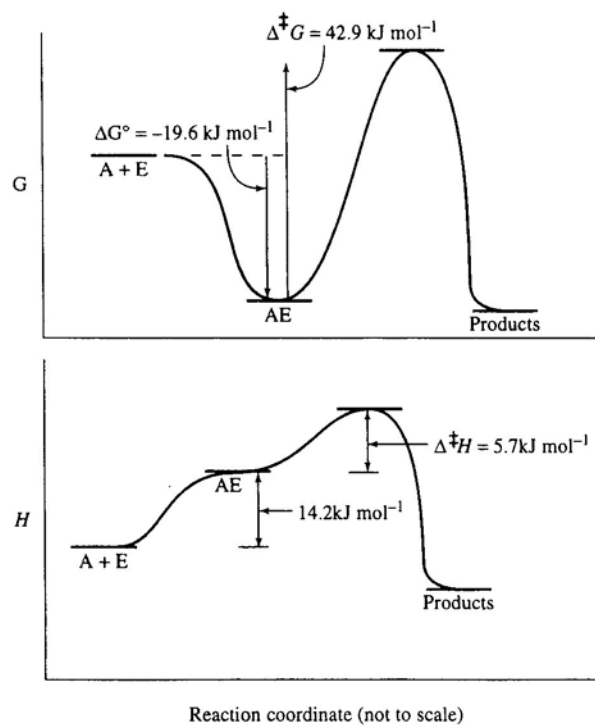
$$\Delta G^\circ = -19.6 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = 14.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = \frac{\Delta G^\circ + \Delta H^\circ}{T} = \frac{14\,219 + 19\,551}{298.15} = 113.265 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S^\circ = 113.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

c)



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\*10.38. The following data relate to an enzyme reaction:

$10^3[\text{s}]/\text{mol dm}^3$	$10^5V/\text{mol dm}^3 \text{ s}^{-1}$
2.0	13
4.0	20
8.0	29
12.0	33
16.0	36
20.0	38

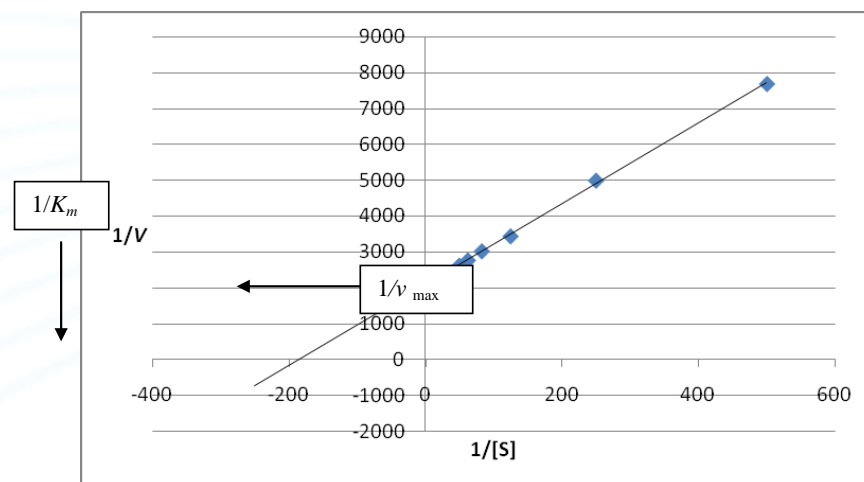
The concentration of the enzyme is  $2.0 \text{ g dm}^{-3}$ , and its molecular weight is  $50\,000 \text{ g/mol}$ . Calculate  $K_m$ , the maximum rate  $V$ , and  $k_c$ .

**Solution:**

Given:  $C = 2.0 \text{ g dm}^{-3}$ ,  $M = 50\,000 \text{ g mol}^{-1}$

Required: determine  $K_m$ , the maximum rate  $V$ , and  $k_c$ .

$10^3[\text{s}] (\text{mol dm}^{-3})$	$10^5V (\text{mol dm}^{-3} \text{ s}^{-1})$	$1/[\text{s}] (1/\text{mol dm}^{-3})$	$1/V (1/\text{mol dm}^{-3} \text{ s}^{-1})$
2	13	500	7692
4	20	250	5000
8	29	125	3448
12	33	083	3030
16	36	62.5	2778
20	38	50.0	2630



The equation of the line generated is:

$$y = 11.291x + 2081.8$$

This means that  $1/v_{\max}$  is equal to the y-intercept, thus,

$$1/v_{\max} = 2081.8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}$$

$$v_{\max} = 1 / 2081.8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}$$

$$v_{\max} = 4.804 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Conversely, the value for  $1/K_m$  is equal to the x-intercept which can be determined by looking at the plot above (or by setting  $y = 0$  and solving for  $x$ ).



$$y = 11.291x + 2081.8$$

$$11.291x + 2081.8 = 0$$

$$11.291x = -2081.8$$

$$x = \frac{-2081.8}{11.291}$$

$$x = 1 / K_m = -184.3769374$$

$$K_m = |-184.3769374|^{-1}$$

$$\boxed{K_m = 5.42 \times 10^{-3} \text{ mol dm}^{-3}}$$

It should be remembered that the Eq. 10.82 is not always the best way to represent the rate for a particular reaction. When we know that the Michaelis-Menten equation can be applied but we are unsure of the mechanism, we should use Eq. 10.85 which state that:

$$v = \frac{k_c [E]_o [S]}{K_m + [S]}$$

It is possible to then say that,

$$v_{\max} = k_c [E]_o$$

$$k_c = \frac{v_{\max}}{[E]_o}$$

Let us now determine the value of the enzyme concentration.

$$[E]_o = \frac{2 \text{ g dm}^{-3}}{50\,000 \text{ g mol}^{-1}}$$

$$[E]_o = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$$

$$k_c = \frac{4.804 \times 10^{-4} \cancel{\text{mol dm}^{-3}} \text{ s}^{-1}}{4.0 \times 10^{-5} \cancel{\text{mol dm}^{-3}}}$$

$$\boxed{k_c = 12.01 \text{ s}^{-1}}$$

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**10.39.** The following data have been obtained for the myosin-catalyzed hydrolysis of ATP.

Temperature/°C	$k_c \times 10^6/\text{s}^{-1}$
39.9	4.67
43.8	7.22
47.1	10.0
50.2	13.9

Calculate, at 40 °C, the energy of activation, the enthalpy of activation, the Gibbs energy of activation, and the entropy of activation.

**Solution:**

Given: see table above

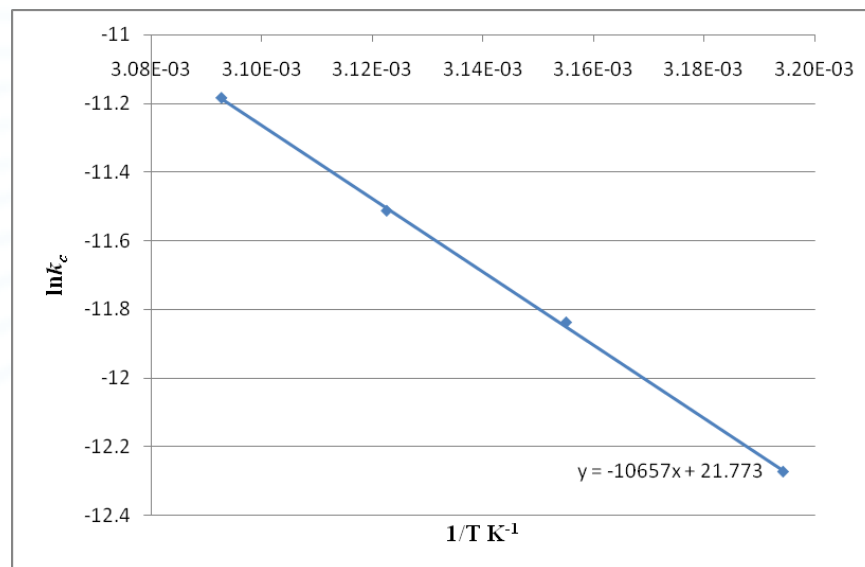
Required:  $\Delta^\ddagger H^\circ$ ,  $\Delta^\ddagger S^\circ$ , and  $\Delta^\ddagger G^\circ$  at 40 °C

Recall that,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

So we can plot  $\ln k$  vs.  $\frac{1}{T}$  in order to determine the activation energy (which appears in the slope portion of the equation for the line). The  $k$  that will be used is actually  $k_c$ .



T / °C	T / K	1/T K <sup>-1</sup>	k <sub>c</sub> / s <sup>-1</sup>	ln k <sub>c</sub>
39.90	313.05	3.19E-03	4.67E-06	-12.274
43.80	316.95	3.16E-03	7.22E-06	-11.839
47.10	320.25	3.12E-03	1.00E-05	-11.513
50.20	323.35	3.09E-03	1.39E-05	-11.184

From the equation of the line, we see that the slope is  $m = -10\,657$ . From this, we can determine the activation energy.

$$m = -10\,567 = -\frac{E_a}{R}$$

$$E_a = (-10\,567 \text{ K}) \left( -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right)$$

$$E_a = 87\,859 \text{ J mol}^{-1}$$

$$E_a = 87.9 \text{ kJ mol}^{-1}$$

From the previous chapter we know that,

$$\Delta^\ddagger H^\circ = E_a - RT \text{ therefore,}$$

$$\Delta^\ddagger H^\circ = 87\,859 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(313.15 \text{ K})$$

$$\Delta^\ddagger H^\circ = 85\,255 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger H^\circ = 85.26 \text{ kJ mol}^{-1}}$$

Also, we know that,

$$k_c = \frac{k_B T}{h} e^{-\frac{\Delta^\ddagger G^\circ}{RT}}$$

Which can be rearranged to solve for  $\Delta^\ddagger G^\circ$ .

$$\ln k_c = \ln \frac{k_B T}{h} - \frac{\Delta^\ddagger G^\circ}{RT}$$

$$\frac{\Delta^\ddagger G^\circ}{RT} = \ln \frac{k_B T}{h} - \ln k_c$$

$$\Delta^\ddagger G^\circ = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(313.15 \text{ K}) \left( \ln \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(313.15 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})} - \ln(4.72 \times 10^{-6} \text{ s}^{-1}) \right)$$

$$\Delta^\ddagger G^\circ = (2603.686 \text{ J mol}^{-1})(41.771)$$

$$\Delta^\ddagger G^\circ = 108\,758 \text{ J mol}^{-1}$$

$$\boxed{\Delta^\ddagger G^\circ = 108.8 \text{ kJ mol}^{-1}}$$

Using the equation  $\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$  we can determine the value for the entropy of activation.

$$T\Delta^\ddagger S^\circ = \Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ$$

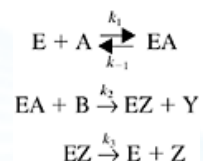
$$\Delta^\ddagger S^\circ = \frac{\Delta^\ddagger H^\circ - \Delta^\ddagger G^\circ}{T}$$

$$\Delta^\ddagger S^\circ = \frac{(85\,255 - 108\,758) \text{ J mol}^{-1}}{313.15 \text{ K}}$$

$$\Delta^\ddagger S^\circ = -75.05 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

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**\*10.40.** The following is a simplified version of the mechanism that has been proposed by H. Theorell and Britton Chance for certain enzyme reactions involving two substrates A and B.



Assume that the substrates A and B are in excess of E so that the steady-state treatment can be applied to EA and EZ, and obtain an expression for the rate.

**Solution:**

Given: see above

Required: overall rate equation

Applying the steady-state approximation for EA, we obtain,

$$\frac{d[\text{EA}]}{dt} = v_{\text{EA}} = k_1[\text{E}][\text{A}] - k_{-1}[\text{EA}] - k_2[\text{EA}][\text{B}]$$

$$\frac{d[\text{EA}]}{dt} = 0$$

$$k_1[\text{E}][\text{A}] - k_{-1}[\text{EA}] - k_2[\text{EA}][\text{B}] = 0$$

Applying the steady-state approximation for EZ, we obtain,

$$\frac{d[\text{EZ}]}{dt} = v_{\text{EZ}} = k_2[\text{EA}][\text{B}] - k_3[\text{EZ}]$$

$$\frac{d[\text{EZ}]}{dt} = 0$$

$$k_2[\text{EA}][\text{B}] - k_3[\text{EZ}] = 0$$

We can now formulate an equation representing the initial concentration of the enzyme.

$$[E]_o = [E] + [EA] + [EZ]$$

With this, it is obvious that the steady-state approximation for EA should be solved for E so that it can be expressed in terms of EA and substituted into the equation for the initial concentration of the enzyme.

$$k_1[E][A] = k_{-1}[EA] + k_2[EA][B]$$

$$[E] = \frac{k_{-1}[EA] + k_2[EA][B]}{k_1[A]}$$

$$[E]_o = \frac{k_{-1}[EA] + k_2[EA][B]}{k_1[A]} + [EA] + [EZ]$$

The steady-state approximation for EZ should be solved for EZ in order to express it in terms of EA which can also be substituted into the equation representing the initial concentration of the enzyme.

$$k_2[EA][B] = k_3[EZ]$$

$$[EZ] = \frac{k_2[EA][B]}{k_3}$$

$$[E]_o = \frac{k_{-1}[EA] + k_2[EA][B]}{k_1[A]} + [EA] + \frac{k_2[EA][B]}{k_3}$$

The final expression above can be factored which yields,

$$[E]_o = [EA] \left\{ \frac{k_{-1} + k_2[B]}{k_1[A]} + 1 + \frac{k_2[B]}{k_3} \right\}$$

The overall rate is given by,

$$v = k_2[EA][B]$$

Therefore,



$$[EA] = \frac{[E]_o}{\left\{ \frac{k_{-1} + k_2[B]}{k_1[A]} + 1 + \frac{k_2[B]}{k_3} \right\}}$$

$$v = k_2 \frac{[E]_o}{\left\{ \frac{k_{-1} + k_2[B]}{k_1[A]} + 1 + \frac{k_2[B]}{k_3} \right\}} [B]$$

$$v = \frac{k_2 [E]_o [B]}{\left\{ \frac{k_{-1} + k_2[B]}{k_1[A]} + 1 + \frac{k_2[B]}{k_3} \right\}}$$

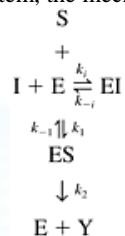
This can be simplified to the following expression:

$$v = \frac{k_1 k_2 k_3 [A] [E]_o [B]}{k_{-1} k_3 + k_1 k_3 [A] + k_2 k_3 [B] + k_1 k_2 [A] [B]}$$

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\*10.41. When an inhibitor I is added to a single-substrate enzyme system, the mechanism is sometimes:



This is known as a *competitive* mechanism, since S and I compete for sites on the enzyme.

a. Assume that the substrate and inhibitor are present in great excess of the enzyme, apply the steady-state treatment, and obtain the rate equation.

b. Obtain an expression for the degree of inhibition defined as:

$$\epsilon = \frac{v_0 - v}{v_0}$$

where  $v$  is the rate in the presence of inhibitor and  $v_0$  is the rate in its absence.

**Solution:**

a) We will apply the steady-state approximation to both ES and EI.

$$\frac{d[\text{ES}]}{dt} = v_{\text{ES}} = k_1[\text{S}][\text{E}] - k_{-1}[\text{ES}] - k_2[\text{ES}]$$

$$\frac{d[\text{ES}]}{dt} = 0$$

$$k_1[\text{S}][\text{E}] - k_{-1}[\text{ES}] - k_2[\text{ES}] = 0$$

$$\frac{d[\text{EI}]}{dt} = v_{\text{EI}} = k_i[\text{I}][\text{E}] - k_{-i}[\text{EI}]$$

$$\frac{d[\text{EI}]}{dt} = 0$$

$$k_i[\text{I}][\text{E}] - k_{-i}[\text{EI}] = 0$$

Solving the first equation for ES we obtain,

$$[ES] = \frac{k_1 [S][E]}{k_{-1} + k_2}$$

Solving the second equation for EI we obtain,

$$k_i [I][E] = k_{-i} [EI]$$

$$[EI] = \frac{k_i [I][E]}{k_{-i}}$$

Solving the first equation again but this time in order to isolate E;

$$k_1 [S][E] = k_{-1} [ES] + k_2 [ES]$$

$$k_1 [S][E] = [ES](k_{-1} + k_2)$$

$$[E] = \frac{[ES](k_{-1} + k_2)}{k_1 [S]}$$

The initial enzyme concentration is given by,

$$[E]_o = [E] + [ES] + [EI]$$

Substituting the expressions found for E, ES and EI we obtain to following:

$$[E]_o = \frac{[ES](k_{-1} + k_2)}{k_1 [S]} + [ES] + \frac{k_i [I][E]}{k_{-i}}$$

However, we can see here that we cannot further simplify this expression due to the presence of E. In order to eliminate this term, we can perform the following operations:

$$[EI] = \frac{k_i [I] \frac{[ES](k_{-1} + k_2)}{k_1 [S]}}{k_{-i}}$$

$$[EI] = \frac{k_i [I][ES](k_{-1} + k_2)}{k_{-i} k_1 [S]}$$

$$[E]_o = \frac{[ES](k_{-1} + k_2)}{k_1 [S]} + [ES] + \frac{k_i [I][ES](k_{-1} + k_2)}{k_{-i} k_1 [S]}$$

We will now factor out the ES term to obtain,

$$[E]_o = [ES] \left\{ \frac{(k_{-1} + k_2)}{k_1 [S]} + 1 + \frac{k_i [I](k_{-1} + k_2)}{k_{-i} k_1 [S]} \right\}$$

The overall rate equation is given by,

$$v = k_2 [ES]$$

Written in terms of the initial concentration of enzyme the rate equation becomes,

$$v = \frac{k_2 [E]_o}{\frac{(k_{-1} + k_2)}{k_1 [S]} + 1 + \frac{k_i [I](k_{-1} + k_2)}{k_{-i} k_1 [S]}}$$

It is possible to further simplify the denominator by multiplying all terms by the concentration S.

$$v = \frac{k_2 [E]_o [S]}{\frac{(k_{-1} + k_2)}{k_1} + [S] + \frac{[I] k_i (k_{-1} + k_2)}{k_{-i} k_1}}$$

Let us combine the terms in the denominator,

$$\frac{(k_{-1} + k_2)}{k_1} + \frac{k_i (k_{-1} + k_2)}{k_{-i} k_1} [I] + [S]$$

Recall that,  $\frac{(k_{-1} + k_2)}{k_1} = K_m$  and  $K_i = \frac{k_{-i}}{k_i}$  therefore,

$$K_m \left( 1 + \frac{[I]}{K_i} \right) + [S]$$

$$v = \frac{k_2 [E]_o [S]}{K_m \left( 1 + \frac{[I]}{K_i} \right) + [S]}$$

b) Given that  $\epsilon = \frac{v_0 - v}{v_0}$ ,

$$\epsilon = \frac{v_0}{v_0} - \frac{v}{v_0} \rightarrow 1 - \frac{v}{v_0}$$

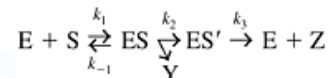
$$\epsilon = 1 - \frac{\frac{k_2 [E]_o [S]}{K_m \left( 1 + \frac{[I]}{K_i} \right) + [S]}}{\frac{k_2 [E]_o [S]}{K_m + [S]}} \rightarrow \frac{K_m + [S]}{k_2 [E]_o [S]} \times \frac{k_2 [E]_o [S]}{K_m \left( 1 + \frac{[I]}{K_i} \right) + [S]}$$

$$\epsilon = 1 - \frac{K_m + [S]}{K_m \left( 1 + \frac{[I]}{K_i} \right) + [S]}$$

$$\epsilon = \frac{\frac{K_m}{K_i} [I]}{K_m \left( 1 + \frac{[I]}{K_i} \right) + [S]}$$

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\*10.42. Obtain the rate equation corresponding to the mechanism:



Assume ES and ES' to be in the steady state and the substrate concentration to be much higher than the enzyme concentration. Express the catalytic constant  $k_c$  and the Michaelis constant  $K_m$  in terms of  $k_1$ ,  $k_{-1}$ ,  $k_2$ , and  $k_3$ .

**Solution:**

Given: see mechanism above

Required: overall rate equation

We will solve this problem in a similar manner as we did for the previous one. Let us begin by applying the steady-state treatment for ES and ES'.

$$\frac{d[\text{ES}]}{dt} = v_{\text{ES}} = k_1 [\text{S}][\text{E}] - k_{-1} [\text{ES}] - k_2 [\text{ES}]$$

$$\frac{d[\text{ES}]}{dt} = 0$$

$$k_1 [\text{S}][\text{E}] = k_{-1} [\text{ES}] + k_2 [\text{ES}]$$

$$k_1 [\text{S}][\text{E}] = [\text{ES}](k_{-1} + k_2)$$

$$[\text{ES}] = \frac{k_1 [\text{S}][\text{E}]}{k_{-1} + k_2}$$

$$[\text{E}] = \frac{[\text{ES}](k_{-1} + k_2)}{k_1 [\text{S}]}$$

$$\frac{d[\text{ES}']}{dt} = v_{\text{ES}'} = k_2 [\text{ES}] - k_3 [\text{ES}']$$

$$\frac{d[\text{ES}']}{dt} = 0$$

$$k_2 [\text{ES}] = k_3 [\text{ES}']$$

$$[\text{ES}'] = \frac{k_2 [\text{ES}]}{k_3}$$

$$[\text{E}]_0 = [\text{E}] + [\text{ES}] + [\text{ES}']$$

$$[\text{E}]_0 = \frac{[\text{ES}](k_{-1} + k_2)}{k_1 [\text{S}]} + [\text{ES}] + \frac{k_2 [\text{ES}]}{k_3}$$

$$[\text{E}]_0 = [\text{ES}] \left\{ \frac{(k_{-1} + k_2)}{k_1 [\text{S}]} + 1 + \frac{k_2}{k_3} \right\}$$

The overall rate equation is given by,



$$v = k_2 [\text{ES}]$$

$$v = \frac{k_2 [\text{E}]_0}{\frac{(k_{-1} + k_2)}{k_1 [\text{S}]} + 1 + \frac{k_2}{k_3}}$$

$$v = \frac{\frac{k_2 k_3}{k_2 + k_3} [\text{E}]_0 [\text{S}]}{\frac{k_{-1} + k_2}{k_1} \frac{k_3}{k_2 + k_3} + [\text{S}]}$$

When  $[\text{S}]$  is large

$$v = \frac{k_1 k_2}{k_{-1} + k_2} [\text{E}]_0$$

and the catalytic constant is therefore

$$k_c = \frac{k_1 k_2}{k_{-1} + k_2}$$

$K_m$  is the first term in the denominator of the rate equation:

$$K_m = \frac{k_{-1} + k_2}{k_1} \frac{k_3}{k_2 + k_3}$$

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**\*10.43.** Enzyme-catalyzed reactions frequently follow an equation of the form of Eq. 10.85. Suppose that  $k_c$  and  $K_m$  show the following temperature dependence:

$$k_c = A_c \exp(-E_c/RT) \text{ and } K_m = B \exp(-\Delta H_m/RT)$$

where  $A_c$ ,  $B$ ,  $E_c$ , and  $\Delta H_m$  are temperature-independent parameters. Explain under what conditions, with  $[S]$  held constant, the rate may pass through a maximum as the temperature is raised.

**Solution:**

Given: Eq. 10.85,  $k_c = A_c \exp(-E_c/RT)$  and  $K_m = B \exp(-\Delta H_m/RT)$

Required: when is  $[S]$  held constant?

Suppose that  $\Delta H_m$  is positive:

$K_m$  will then increase accordingly with an increase in temperature (linearly) and at sufficiently low temperature it will be much smaller than the concentration of the substrate. The effective activation energy is therefore given by  $E_c$  and its rate will increase as the temperature increases.

At sufficiently high temperatures,  $K_m$  will be much larger than the concentration of the substrate and the effective activation energy will be given by  $E_c - \Delta H_m$ .

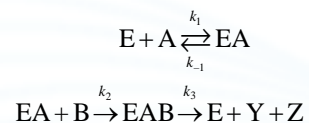
If  $\Delta H_m$  is larger than  $E_c$ , effective activation energy will be negative. This would mean that the rate has gone through a maximum as the temperature was increased.

If  $\Delta H_m$  is smaller than  $E_c$ , effective activation energy will be positive. This does not indicate that the rate has gone through a maximum! However, the observed activation energy will be lower at higher temperatures. An Arrhenius plot will therefore show curvature (ie. bending away from the axes).

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**10.44.** Some enzyme reactions involving two substrates A and B occur by the following mechanism:



(This is known as the *ordered ternary-complex mechanism*; A must add first to E, and the resulting complex EA reacts with B; the complex EB is not formed.)

The concentrations of A and B are much greater than the concentration of E. Apply the steady-state treatment and obtain an expression for the rate.

**Solution:**

Since we are told that the concentrations of A and B are much greater than the concentration E, we can apply the steady-state treatment to complexes EA and EAB.

$$\frac{d[\text{EA}]}{dt} = v_{\text{EA}} = k_1[\text{E}][\text{A}] - k_{-1}[\text{EA}] - k_2[\text{EA}][\text{B}]$$

$$\frac{d[\text{EA}]}{dt} = 0$$

$$k_1[\text{E}][\text{A}] = k_{-1}[\text{EA}] + k_2[\text{EA}][\text{B}]$$

$$k_1[\text{E}][\text{A}] = [\text{EA}](k_{-1} + k_2[\text{B}])$$

$$[\text{EA}] = \frac{k_1[\text{E}][\text{A}]}{(k_{-1} + k_2[\text{B}])}$$

$$[\text{E}] = \frac{[\text{EA}](k_{-1} + k_2[\text{B}])}{k_1[\text{A}]}$$

$$\frac{d[\text{EAB}]}{dt} = v_{\text{EAB}} = k_2[\text{EA}][\text{B}] - k_3[\text{EAB}]$$

$$\frac{d[\text{EAB}]}{dt} = 0$$

$$k_2[\text{EA}][\text{B}] = k_3[\text{EAB}]$$

$$[\text{EAB}] = \frac{k_2[\text{EA}][\text{B}]}{k_3}$$

$$[\text{EA}] = \frac{k_3[\text{EAB}]}{k_2[\text{B}]}$$

Since  $[\text{E}]_0 = [\text{E}] + [\text{EA}] + [\text{EAB}]$  then we can write:

$$[\text{E}]_0 = \frac{[\text{EA}](k_{-1} + k_2[\text{B}])}{k_1[\text{A}]} + \frac{k_3[\text{EAB}]}{k_2[\text{B}]} + [\text{EAB}]$$

$$[\text{E}]_0 = \frac{\frac{k_3[\text{EAB}]}{k_2[\text{B}]}(k_{-1} + k_2[\text{B}])}{k_1[\text{A}]} + \frac{k_3[\text{EAB}]}{k_2[\text{B}]} + [\text{EAB}]$$

$$[\text{E}]_0 = \frac{k_3[\text{EAB}](k_{-1} + k_2[\text{B}])}{k_2[\text{B}]k_1[\text{A}]} + \frac{k_3[\text{EAB}]}{k_2[\text{B}]} + [\text{EAB}]$$

$$[\text{E}]_0 = [\text{EAB}] \left\{ \frac{k_3(k_{-1} + k_2[\text{B}])}{k_2[\text{B}]k_1[\text{A}]} + \frac{k_3}{k_2[\text{B}]} + 1 \right\}$$

The overall rate equation is given by,

$$v = k_3[\text{EAB}]$$

Which can be written in the following manner:

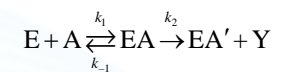
$$[\text{EAB}] = \frac{[\text{E}]_0}{\frac{k_3(k_{-1} + k_2[\text{B}])}{k_2[\text{B}]k_1[\text{A}]} + \frac{k_3}{k_2[\text{B}]} + 1}$$

$$v = \frac{k_3[\text{E}]_0}{\frac{k_3(k_{-1} + k_2[\text{B}])}{k_2[\text{B}]k_1[\text{A}]} + \frac{k_3}{k_2[\text{B}]} + 1}$$

$$v = \frac{k_1k_2k_3[\text{E}]_0[\text{A}][\text{B}]}{k_3(k_{-1} + k_2[\text{B}]) + k_3k_1[\text{A}] + k_1k_2[\text{B}][\text{A}]}$$

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- 10.45.** The following “ping-pong” mechanism appears sometimes to apply to an enzyme-catalyzed reaction between two substrates A and B to give the final products Y and Z:



It can be assumed that the substrates are present in great excess of the enzyme and that steady-state conditions apply. Obtain an expression for the rate of reaction.

**Solution:**

Let us apply the steady-state approximation to EA, EA' and EA'B. This procedure yields;

$$\frac{d[\text{EA}]}{dt} = v_{\text{EA}} = k_1[\text{E}][\text{A}] - k_{-1}[\text{EA}] - k_2[\text{EA}]$$

$$\frac{d[\text{EA}]}{dt} = 0$$

$$k_1[\text{E}][\text{A}] - k_{-1}[\text{EA}] - k_2[\text{EA}] = 0$$

$$k_1[\text{E}][\text{A}] = k_{-1}[\text{EA}] + k_2[\text{EA}]$$

$$k_1[\text{E}][\text{A}] = [\text{EA}](k_{-1} + k_2)$$

$$\frac{d[\text{EA}']}{dt} = v_{\text{EA}'} = k_2[\text{EA}] - k_3[\text{EA}'][\text{B}]$$

$$\frac{d[\text{EA}']}{dt} = 0$$

$$k_2[\text{EA}] - k_3[\text{EA}'][\text{B}] = 0$$

$$k_2[\text{EA}] = k_3[\text{EA}'][\text{B}]$$

$$\frac{d[\text{EA'B}]}{dt} = v_{\text{EA'B}} = k_3[\text{EA}'][\text{B}] - k_4[\text{EA'B}]$$

$$\frac{d[\text{EA'B}]}{dt} = 0$$

$$k_3[\text{EA}'][\text{B}] - k_4[\text{EA'B}] = 0$$

$$k_3[\text{EA}'][\text{B}] = k_4[\text{EA'B}]$$

Since the overall rate equation is given by,

$$v = k_4[\text{EA'B}]$$

We should define the initial enzyme concentration in terms as of EA' but making the appropriate substitutions and rearrangements.

$$[E]_o = [E] + [EA] + [EA'] + [EA'B]$$

$$k_1[E][A] = [EA](k_{-1} + k_2)$$

$$[E] = \frac{[EA](k_{-1} + k_2)}{k_1[A]}$$

$$k_2[EA] = k_3[EA'][B]$$

$$[EA] = \frac{k_3[EA'][B]}{k_2}$$

$$k_3[EA'][B] = k_4[EA'B]$$

$$[EA'B] = \frac{k_3[EA'][B]}{k_4}$$

$$[E]_o = \frac{[EA](k_{-1} + k_2)}{k_1[A]} + \frac{k_3[EA'][B]}{k_2} + [EA'] + \frac{k_3[EA'][B]}{k_4}$$

Since the first term does not involve EA', we will need to make a second substitution.

$$\frac{[EA](k_{-1} + k_2)}{k_1[A]} \rightarrow \frac{\frac{k_3[EA'][B]}{k_2}(k_{-1} + k_2)}{k_1[A]} = \frac{k_3(k_{-1} + k_2)[EA'][B]}{k_2k_1[A]} \quad \text{or} \quad [EA'] \frac{(k_{-1} + k_2)}{k_1[A]} \times \frac{k_3[B]}{k_2}$$

$$\text{thus, } [E]_o = [EA'] \frac{(k_{-1} + k_2)}{k_1[A]} \times \frac{k_3[B]}{k_2} + \frac{k_3[EA'][B]}{k_2} + [EA'] + \frac{k_3[EA'][B]}{k_4}$$

$$[E]_o = [EA'] \left\{ \frac{(k_{-1} + k_2)}{k_1[A]} \times \frac{k_3[B]}{k_2} + \frac{k_3[B]}{k_2} + 1 + \frac{k_3[B]}{k_4} \right\}$$

The overall rate equation is given by,

$$v = k_3[EA'][B]$$



$$v = \frac{k_3 [E]_o [B]}{\frac{(k_{-1} + k_2)}{k_1 [A]} \times \frac{k_3 [B]}{k_2} + \frac{k_3 [B]}{k_2} + 1 + \frac{k_3 [B]}{k_4}}$$

Simplification yields,

$$v = \frac{k_1 k_2 k_3 k_4 [E]_o [A] [B]}{k_1 k_2 k_4 [A] + k_3 k_4 (k_{-1} + k_2) [B] + k_1 k_3 (k_2 + k_4) [A] [B]}$$

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**10.46.** The polymerization of styrene [M] catalyzed by benzoyl peroxide [C] obeys a kinetic equation of the form:

Obtain an expression for the kinetic chain length, in terms of [M], [C], and the rate constants for initiation, propagation, and termination.

**Solution:**

Given:  $-\frac{d[M]}{dt} = k[M]^{3/2}[C]^{1/2}$

Required: expression for the kinetic chain length

Eq. 10.97,

$$-\frac{d[M]}{dt} = k_p \left( \frac{k_i}{k_t} \right)^{\frac{1}{2}} [M]^{\frac{3}{2}} [C]^{\frac{1}{2}}$$

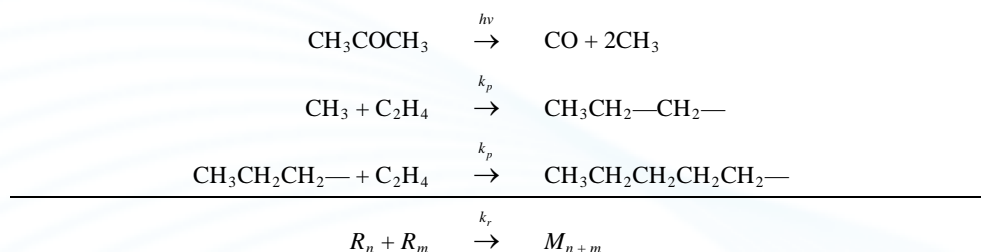
defines the polymerization rate for the rate of initiation,  $\nu_i = k_i [M][C]$  (Eq. 10.96). The chain length is therefore equal to,

$$\frac{k_p [M]^{\frac{1}{2}}}{\left( \frac{k_i}{k_t} [C] \right)^{\frac{1}{2}}}$$

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**10.47.** The polymerization of ethylene [M] photosensitized by acetone occurs by the mechanism:



where one quantum gives  $2\text{CH}_3$ .

Show that the rate equation is:

$$-\frac{d[\text{M}]}{dt} = k_p \left( \frac{2I}{k_t} \right)^{1/2} [\text{M}]$$

where  $I$  is the intensity of light absorbed and  $k_p$  and  $k_t$  are the rate constants for the propagation and termination steps, respectively.

**Solution:**

Given: rate of formation of  $\text{CH}_3$  is  $2I$

Required: see above

The steady-state equations are

$$2I - k_p [\text{CH}_3][\text{M}] - k_t [\text{CH}_3] \sum [\text{R}_n] = 0$$

From Eq. 20.2,

$$k_p [\text{CH}_3][\text{M}] - k_p [\text{CH}_3\text{CH}_2\text{CH}_2\text{—}][\text{M}] - k_t [\text{CH}_3\text{CH}_2\text{CH}_2\text{—}] \sum [\text{R}_n] = 0$$

and so on.

The sum of all the equations is

$$2I - k_t (\sum [\text{R}_n])^2 = 0$$

so that

$$\sum [\text{R}_n] = \left( \frac{2I}{k_t} \right)^{1/2}$$

the rate of removal of monomer is

$$-\frac{d[\text{M}]}{dt} = v = k_p [\text{M}] \sum [\text{R}_n]$$

$$\boxed{-\frac{d[\text{M}]}{dt} = k_p \left( \frac{2I}{k_t} \right)^{1/2} [\text{M}]}$$

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CHAPTER

# 11

Quantum Mechanics  
and Atomic Structure

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LAIDLER . MEISER . SANCTUARY

Physical Chemistry

Electronic Edition

Publisher: MCH Multimedia Inc.

Problems and Solutions

**Chapter 11****Electromagnetic Radiation and Wave Motion**

**11.1.** Calculate, for light of 325 nm wavelength,

- a. the frequency;
- b. the wavenumber;
- c. the photon energy in J, eV, and  $\text{kJ mol}^{-1}$ ; and
- d. the momentum of the photon.

[Solution](#)

**11.2.** A pulsar in the Crab Nebula, NP 0532, emits both radio pulses and optical pulses. A radio pulse is observed at 196.5 Mhz. Calculate

- a. the corresponding wavelength;
- b. the energy of the photon in J, eV and  $\text{J mol}^{-1}$ ; and
- c. the momentum of the photon.

[Solution](#)

**11.3.** The potassium spectrum has an intense doublet with lines at 766.494 nm and 769.901 nm. Calculate the frequency difference between these two lines.

[Solution](#)

**11.4.** Suppose that the position  $y$  of a particle that travels along the  $Y$  axis of a coordinate system is given by

$$y(t) = y_0 \sin \left[ \frac{3\pi \text{ rad}}{5} \left( \frac{t}{s} \right) + C \right]$$

What is the frequency of the wave motion?

[Solution](#)

**11.5.** A mass of 0.2 kg attached to a spring has a period of vibration of 3.0 s.

- a. What is the force constant of the spring?
- b. If the amplitude of vibration is 0.010 m, what is the maximum velocity?

[Solution](#)

\*11.6. If the average energy associated with a standing wave of frequency  $\nu$  in a cavity is

$$\bar{\varepsilon} = \frac{h\nu}{\exp(h\nu/k_{\text{B}}T) - 1}$$

deduce the expression for the low-frequency limit of the average energy associated with the standing wave.

[Solution](#)

### Particles and Waves

11.7. A sodium lamp of 50-watt power emits yellow light at 550 nm. How many photons does it emit each second? What is the momentum of each photon?

[Solution](#)

11.8. The threshold frequency  $\nu_0$  for emission of photoelectrons from metallic sodium was found by Millikan, *Phys. Rev.*, 7, 1916, p. 362, to be  $43.9 \times 10^{13} \text{ s}^{-1}$ . Calculate the work function for sodium. A more recent value, for a carefully outgassed sample of sodium, is  $5.5 \times 10^{13} \text{ s}^{-1}$ . What work function corresponds to that value?

[Solution](#)

11.9. Calculate the value of the de Broglie wavelength associated with

- a. an electron moving with a speed of  $6.0 \times 10^7 \text{ m s}^{-1}$  (this is the approximate velocity produced by a potential difference of 10 kV).
- b. an oxygen molecule moving with a speed of  $425 \text{ m s}^{-1}$  at  $0^\circ\text{C}$ .
- c. an  $\alpha$ -particle emitted by the disintegration of radium, moving at a speed of  $1.5 \times 10^7 \text{ m s}^{-1}$ .
- d. an electron having a speed of  $2.818 \times 10^8 \text{ m s}^{-1}$ .

[Solution](#)

11.10. Consider a colloidal particle with a mass of  $6 \times 10^{-16} \text{ kg}$ . Suppose that its position is measured to within 1.0 nm, which is about the resolving power of an electron microscope. Calculate the uncertainty in the velocity and comment on the significance of the result.

[Solution](#)

**11.11.** Calculate the velocity and the de Broglie wavelength of an electron accelerated by a potential of

- a. 10 V,
- b. 1 kV, and
- c. 1 MV.

[Solution](#)

**\*11.12.** The group velocity of a wave is given by the equation

$$v_g = \frac{dv}{d(1/\lambda)}$$

Prove that the group velocity of a de Broglie particle wave is equal to the ordinary velocity of the particle.

[Solution](#)

**11.13.** Photoelectric experiments show that about 5 eV of energy are required to remove an electron from platinum.

- a. What is the maximum wavelength of light that will remove an electron?
- b. If light of 150 nm wavelength were used, what is the velocity of the emitted electron?

[Solution](#)

**11.14.** Calculate the kinetic energy of an electron that has a wavelength of (a) 10 nm, (b) 100 nm.

[Solution](#)

**11.15.** Calculate the de Broglie wavelength of (a) an  $\alpha$ -particle (a helium nucleus) accelerated by a field of 100 V, and (b) a tennis ball served at 220 km h<sup>-1</sup>. (An  $\alpha$ -particle has a mass of  $6.64 \times 10^{-27}$  kg and a diameter of about  $10^{-15}$  m. A standard tennis ball has a mass of 55.4 g and a diameter of 6.51 cm.)

[Solution](#)



**Quantum-Mechanical Principles**

**11.16.** Assume that the three real functions  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  are normalized and orthogonal. Normalize the following functions:

a.  $\psi_1 + \psi_2$

b.  $\psi_1 - \psi_2$

c.  $\psi_1 + \psi_2 + \psi_3$

d.  $\psi_1 - \frac{1}{\sqrt{2}}\psi_2 + \frac{\sqrt{3}}{\sqrt{2}}\psi_3$

[Solution](#)

**11.17.** Is the function  $Ae^{-ax}$  an eigenfunction of the operator  $d^2/dx^2$ ? If so, what is the eigenvalue?

[Solution](#)

**11.18.** Prove that  $m_1$  must be integral in order for the function

$$\Phi = \sin m_1 \phi$$

to be an acceptable wave function.

[Solution](#)

**11.19.** The energy operator for a time-dependent system (Table 11.1) is

$$i\hbar \frac{\partial}{\partial t}$$

A possible eigenfunction for the system is

$$\Psi(x, y, z, t) = \psi(x, y, z) \exp(-2\pi i E t / \hbar)$$

Show that  $\Psi \Psi^*$ , the probability density, is independent of time.

[Solution](#)

\*11.20. Prove that the momentum operator corresponding to  $p_x$  is a Hermitian operator.

[Solution](#)

11.21. Which of the following functions is an eigenfunction of the operator  $d/dx$ ?

- |              |                 |
|--------------|-----------------|
| a. $k$       | d. $\exp(kx)$   |
| b. $kx^2$    | e. $\exp(kx^2)$ |
| c. $\sin kx$ | f. $\exp(ikx)$  |

( $k$  is a constant, and  $i$  is the square root of minus one.) Give the eigenvalue where appropriate.

[Solution](#)

11.22. Figure 11.20 shows the angular momentum vectors for  $l = 2$  and for  $m = 2, 1, 0, -1, -2$ . In each case, calculate the angles the vectors make with the  $Z$  axis.

[Solution](#)

11.23. Show that the one-electron wave functions  $\psi_{nlm}$  are also eigenfunctions of the operator  $(\hat{L}_x^2 + \hat{L}_y^2)$ . What physical property (observable) is associated with this operator?

[Solution](#)

11.24. Explain why the Heisenberg uncertainty principle would be violated if the harmonic oscillator ground-state energy were zero.

[Solution](#)

### Particle in a Box

11.25. Calculate the lowest possible energy for an electron confined in a cube of sides equal to

- a. 10 pm and
- b. 1 fm (1 femtometre =  $10^{-15}$  m).

The latter cube is the order of magnitude of an atomic nucleus; what do you conclude from the energy you calculate about the probability of a free electron being present in a nucleus?

[Solution](#)

- 11.26.** A particle is moving in one dimension between  $x = a$  and  $x = b$ . The potential energy is such that the particle cannot be outside these limits and that the wave function in between is

$$\psi = A/x$$

- a. Determine the normalization constant  $A$ .
- b. Calculate the average value of  $x$ .

[Solution](#)

- 11.27.** An electron is confined in a one-dimensional box 1 nm long. How many energy levels are there with energy less than 10 eV? How many levels are there with energy between 10 and 100 eV?

[Solution](#)

- 11.28.** Determine whether the eigenfunctions obtained in Section 11.6 for a particle in a one-dimensional box are eigenfunctions for the momentum operator. If they are, obtain the eigenvalues; if they are not, explain why.

[Solution](#)

- \*11.29.** Treat the three-dimensional particle in a box of sides  $a$ ,  $b$ , and  $c$  by analogy with the treatment in Section 11.6. Assume the potential to be zero inside the box and infinite outside, and proceed by the following steps:

- a. Write the basic differential equation that must be solved for the three-dimensional problem.
- b. Separate the equation from (a) into terms involving  $X(x)$ ,  $Y(y)$ , and  $Z(z)$ .
- c. Determine the expressions for  $X$ ,  $Y$ , and  $Z$ .
- d. Obtain the expression (Eq. 11.150) for the total energy.

[Solution](#)

- 11.30.** What is the quantum-mechanical probability of finding the particle in a one-dimensional “box” in the middle third of the “box”? Derive an expression that shows how this quantity depends on the quantum number  $n$ .

[Solution](#)

- 31.** The classical probability for finding a particle in the region  $x$  to  $x + dx$  in a one-dimensional box of length  $a$  is  $dx/a$ .
- a.** Derive the classical probability for finding the particle in the middle third of the box.
  - b.** Show that as  $n \rightarrow \infty$ , the quantum probability obtained in the previous problem becomes identical to the classical result.

[Solution](#)

- \*11.32.** Problem 11.25 is concerned with the calculation of the minimum energy for an electron confined in a cube. Another approach to the problem is to consider, on the basis of the uncertainty principle (Eq. 11.60), the uncertainty in the energy if the uncertainty in the position is equal to the length of the side of the cube. Calculate  $\Delta E$  for a cube of sides equal to

- a.** 10 pm and
- b.** 1 fm ( $10^{-15}$  m),

and compare the results with the minimum energies found for Problem 11.25.

[Solution](#)

- \*11.33.** Prove that any two wave functions for a particle in a one-dimensional box of length  $a$  are orthogonal to each other; that is, they obey the relationship

$$\int_0^a \psi_m \psi_n dx = 0, m \neq n$$

[Solution](#)

- 11.34.** Use the trial function  $\Psi = x(a - x)$  and Eq. 11.247 to calculate an energy for a particle in a one-dimensional box of length  $a$ .

[Solution](#)

- 11.35.** **a.** At a node, a wave function passes through zero. For the problem of the particle in a box, how many nodes are there for  $n = 2$  and  $n = 3$ ?
- b.** From the expression for the radial function for the 3s electron (Table 11.4), obtain expressions for the position of the radial nodes (i.e., the nodes in the solution of the radial equation) in terms of  $Z$  and  $a_0$ .

[Solution](#)

**Vibration and Rotation**

- 11.36.** The vibration frequency of the  $N_2$  molecule corresponds to a wave number of  $2360\text{ cm}^{-1}$ . Calculate the zero-point energy and the energy corresponding to  $v = 1$ .

[Solution](#)

- \*11.37.** If a rigid body rotates in the  $XY$  plane, about the  $Z$  axis, the angular momentum operator is

$$\hat{L} = -i\hbar \frac{\partial}{\partial \phi}$$

(see Figure 11.15). If the moment of inertia is  $I$ , what is the energy operator?

(For additional problems dealing with molecular vibrations and rotations, see Chapter 13.)

[Solution](#)

**The Atom**

- 11.38.** Calculate the ionization energy of the hydrogen atom on the basis of the Bohr theory.

[Solution](#)

- 11.39.** Calculate, on the basis of the Bohr theory, the linear velocity of an electron (mass =  $9.11 \times 10^{-31}\text{ kg}$ ) in the ground state of the hydrogen atom. To what de Broglie wavelength does this velocity correspond? Deduce an equation for the de Broglie wavelength, in a Bohr orbit of quantum number  $n$ , with  $Z = 1$ , in terms of  $a_0$  and  $n$ . What is the ratio of the circumference of a Bohr orbit of quantum number  $n$  to the de Broglie wavelength?

[Solution](#)

- 11.40.** For a hydrogenlike atom (a one-electron system with a charge number of  $Z$ ), find the radius of the sphere on which the probability of finding the  $1s$  electron is a maximum. Compare the result to the expression of Eq. 11.44.

[Solution](#)

**\*11.41.** Calculate the reduced masses of the hydrogen and deuterium atoms, using the following masses for the particles:

Electron:	$9.1095 \times 10^{-31} \text{ kg}$
Proton:	$1.6727 \times 10^{-27} \text{ kg}$
Deuterium nucleus:	$3.3434 \times 10^{-27} \text{ kg}$

**a.** Explain qualitatively what effect the different reduced masses will have on the Bohr radii and therefore on the positions of the lines in the atomic spectra.

**b.** The Balmer spectrum of hydrogen has a line of wavelength 656.47 nm. Deduce the wavelength of the corresponding line in the spectrum of deuterium.

[Solution](#)

**11.42.** Calculate the wavelength and energy corresponding to the  $n = 4$  to  $n = 5$  transition in the hydrogen atom.

[Solution](#)

**11.43.** Calculate, in joules and in atomic units, the potential energy of an electron in the  $n = 2$  orbit of the hydrogen atom.

[Solution](#)

**11.44.** The first ionization energy of the Li atom is 5.39 eV. Estimate an effective nuclear charge  $Z_{\text{eff}}$  for the valence electron in the Li atom.

[Solution](#)

**11.45.** The first ionization energy of the Na atom is 5.14 eV. Estimate the effective nuclear charge  $Z_{\text{eff}}$  for the valence electron in the Na atom.

[Solution](#)

**\*11.46.** Use Slater's method (Section 11.13) to determine the effective nuclear charge for

- a.** a 3s electron in the chlorine atom,
- b.** a 3p electron in the phosphorus atom, and
- c.** the 4s electron in the potassium atom.

[Solution](#)

**\*11.47.** A normalized Slater orbital for the 1s orbital in the helium atom is

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z_{\text{eff}}}{a_0} \right)^{3/2} \exp(-Z_{\text{eff}} r/a_0)$$

where  $Z_{\text{eff}}$  is the effective charge number. It leads to the following expression for the energy

$$E = \frac{e^2}{a_0} \left( Z_{\text{eff}}^2 - \frac{27}{8} Z_{\text{eff}} \right).$$

Treat  $Z_{\text{eff}}$  as a variation parameter, and calculate a minimum energy in terms of  $e$  and  $a_0$ . Why is the optimum value of  $Z_{\text{eff}}$  different from the actual charge number?

[Solution](#)

**\*11.48.** Use the wave function for the 1s orbital of the hydrogen atom, given in Table 11.5, to obtain an expression for the probability that the electron lies between the distance  $r$  and  $r + dr$  from the nucleus. (Use spherical polar coordinates, for which the volume element is  $r^2 dr \sin \theta d\theta d\phi$ .)

[Solution](#)

**\*11.49.** Unsöld's theorem (Section 11.8) states that, for a given value of  $l$ , the sum of the values of

$$\sum_{l,m} [\Theta_{l,m}(\theta) \Phi_m(\phi)]^2$$

is independent of  $\theta$  and  $\phi$ , i.e., is a constant. Write all these functions for the 2p orbitals (see Tables 11.2 and 11.3), and show that their sum shows no angular dependence.

[Solution](#)

**Essay Questions**

- 11.50.** With emphasis on the physical significance, explain precisely what is meant by a *normalized* wave function.
- 11.51.** Explain clearly the relationship between the Heisenberg uncertainty principle and the question of whether two operators commute.
- 11.52.** Give an account of the main principles underlying the variation method in quantum mechanics.
- 11.53.** Discuss the reasons for abandoning the Bohr theory of the atom.



**Solutions**

**11.1.** Calculate, for light of 325 nm wavelength,

- a. the frequency;
- b. the wavenumber;
- c. the photon energy in J, eV, and  $\text{kJ mol}^{-1}$ ; and
- d. the momentum of the photon.

**Solution:**

Given:  $\lambda = 325 \text{ nm}$

Required:  $\nu$ ,  $\bar{\nu}$ ,  $\epsilon$ ,  $p$

a. The frequency is calculated from Eq. 11.1

$$\lambda \nu = c$$

$$\nu = \frac{c}{\lambda}$$

$$\nu = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{325 \times 10^{-9} \text{ m}}$$

$$\nu = 9.224\,615\,385 \times 10^{14} \text{ s}^{-1}$$

$$\boxed{\nu = 9.22 \times 10^{14} \text{ s}^{-1}}$$

b. The wavenumber is given by the inverse of the wavelength.

$$\bar{\nu} = \frac{1}{\lambda}$$

$$\bar{\nu} = \frac{1}{325 \times 10^{-7} \text{ cm}}$$

$$\bar{\nu} = 30\,769.230\,77 \text{ cm}^{-1}$$

$$\boxed{\bar{\nu} = 30.8 \times 10^4 \text{ cm}^{-1}}$$

c. The photon energy is given by in the *Key Equations* section as

$$E = h\nu$$

$$\varepsilon = (6.626 \times 10^{-34} \text{ J s}) (9.224\,615\,385 \times 10^{14} \text{ s}^{-1})$$

$$\varepsilon = 6.112\,230\,15 \times 10^{-19} \text{ J}$$

$$\boxed{\varepsilon = 6.11 \times 10^{-19} \text{ J}}$$

In electron volts we get,

$$\varepsilon = \frac{6.112\,230\,15 \times 10^{-19} \text{ J}}{1.602 \times 10^{-19} \text{ J eV}^{-1}}$$

$$\varepsilon = 3.815\,374\,628 \text{ eV}$$

$$\boxed{\varepsilon = 3.82 \text{ eV}}$$

In kJ per mole we get,

$$\varepsilon = (6.112\,230\,15 \times 10^{-19} \text{ J}) (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$\varepsilon = 368\,078.499\,9 \text{ J mol}^{-1}$$

$$\boxed{\varepsilon = 368 \text{ kJ mol}^{-1}}$$

d. The momentum is given by Eq. 11. 55

$$\lambda = \frac{h}{p}$$

$$p = \frac{6.626 \times 10^{-34} \text{ J s}}{325 \times 10^{-9} \text{ m}}$$

$$p = 2.038\,769\,23 \times 10^{-27} \text{ kg m s}^{-1}$$

$$\boxed{p = 2.04 \times 10^{-27} \text{ kg m s}^{-1}}$$

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**11.2.** A pulsar in the Crab Nebula, NP 0532, emits both radio pulses and optical pulses. A radio pulse is observed at 196.5 Mhz. Calculate

- the corresponding wavelength;
- the energy of the photon in J, eV and  $\text{J mol}^{-1}$ ; and
- the momentum of the photon.

**Solution:**

Given:  $\nu = 196.5 \text{ Mhz}$

Required:  $\lambda$ ,  $\varepsilon$ ,  $p$

e. The wavelength is calculated from Eq. 11.1

$$\lambda \nu = c$$

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m } \cancel{\text{s}^{-1}}}{196.5 \times 10^6 \cancel{\text{ s}^{-1}}}$$

$$\lambda = 1.525\,699\,746 \text{ m}$$

$$\boxed{\lambda = 1.526 \text{ m}}$$

f. The photon energy is given by in the *Key Equations* section as

$$E = h\nu$$

$$\varepsilon = (6.626 \times 10^{-34} \text{ J } \cancel{\text{s}}) (196.5 \times 10^6 \cancel{\text{ s}^{-1}})$$

$$\varepsilon = 1.302\,009 \times 10^{-25} \text{ J}$$

$$\boxed{\varepsilon = 1.302 \times 10^{-25} \text{ J}}$$

In electron volts we get,

$$\varepsilon = \frac{1.302\,009 \times 10^{-25} \text{ J}}{1.602 \times 10^{-19} \text{ eV}^{-1}}$$

$$\varepsilon = 8.127\,397\,004 \times 10^{-7} \text{ eV}$$

$$\boxed{\varepsilon = 8.127 \times 10^{-7} \text{ eV}}$$

In kJ per mole we get,

$$\varepsilon = (1.302\,009 \times 10^{-25} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$\varepsilon = 0.078\,406\,982 \text{ J mol}^{-1}$$

$$\boxed{\varepsilon = 7.841 \times 10^{-2} \text{ kJ mol}^{-1}}$$

g. The momentum is given by Eq. 11. 55

$$\lambda = \frac{h}{p}$$

$$p = \frac{6.626 \times 10^{-34} \text{ J s}}{1.525\,699\,746 \text{ m}}$$

$$p = 4.342\,925\,28 \times 10^{-34} \text{ kg m s}^{-1}$$

$$\boxed{p = 4.343 \times 10^{-34} \text{ kg m s}^{-1}}$$

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**11.3.** The potassium spectrum has an intense doublet with lines at 766.494 nm and 769.901 nm. Calculate the frequency difference between these two lines.

**Solution:**

Given:  $\lambda_1 = 766.494 \text{ nm}$ ,  $\lambda_2 = 769.901 \text{ nm}$

Required:  $\Delta \nu$

The frequency difference is calculated by converting the wavelengths to their respective frequencies. Using Eq. 11.1,

$$\lambda \nu = c$$

$$\nu = \frac{c}{\lambda}$$

$$\nu_1 = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{766.494 \times 10^{-9} \text{ m}}$$

$$\nu_1 = 3.911315679 \times 10^{14} \text{ s}^{-1}$$

$$\nu_2 = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{769.901 \times 10^{-9} \text{ m}}$$

$$\nu_2 = 3.894007152 \times 10^{14} \text{ s}^{-1}$$

$$\Delta \nu = \nu_1 - \nu_2$$

$$\Delta \nu = 3.911315679 \times 10^{14} \text{ s}^{-1} - 3.894007152 \times 10^{14} \text{ s}^{-1}$$

$$\Delta \nu = 1.730852735 \times 10^{12} \text{ s}^{-1}$$

$$\boxed{\Delta \nu = 1.731 \times 10^{12} \text{ s}^{-1}}$$

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**11.4.** Suppose that the position  $y$  of a particle that travels along the  $Y$  axis of a coordinate system is given by

$$y(t) = y_0 \sin \left[ \frac{3\pi \text{ rad}}{5} \left( \frac{t}{s} \right) + C \right]$$

What is the frequency of the wave motion?

**Solution:**

Given: equation above

Required:  $\nu$

To find the frequency, we compare this equation to that given by Eq. 11.6,

$$y = A \sin(\omega t + \delta)$$

Angular frequency is defined in Eq. 11.4 as

$$\omega = (2\pi \text{ rad})\nu$$

Therefore frequency is obtained as,

$$\nu = \frac{\omega}{2\pi \text{ rad}}$$

$$\nu = \frac{3\cancel{\pi}/5 \text{ rad s}^{-1}}{2\cancel{\pi} \text{ rad}}$$

$$\nu = \frac{3}{10} \text{ s}^{-1}$$

$$\boxed{\nu = 0.3 \text{ s}^{-1}}$$

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**11.5.** A mass of 0.2 kg attached to a spring has a period of vibration of 3.0 s.

- a. What is the force constant of the spring?
- b. If the amplitude of vibration is 0.010 m, what is the maximum velocity?

**Solution:**

Given:  $m = 0.2 \text{ kg}$ ,  $\tau = 3.0 \text{ s}$ ,  $A = 0.010 \text{ m}$

Required:  $k_h$ ,  $v_{\max}$

a. The force constant of the spring can be determined using Eq. 11.15

$$v = \frac{1}{2\pi} \sqrt{\frac{k_h}{m}}$$

$$k_h = m(2\pi v)^2$$

The period is the inverse of the frequency, thus,

$$\tau = \frac{1}{v}$$

$$v = \frac{1}{\tau}$$

$$k_h = 0.2 \text{ kg} \left( 2\pi \frac{1}{3.0 \text{ s}} \right)^2$$

$$k_h = 0.877 \, 298 \, 169 \text{ kg s}^{-2}$$

$$\boxed{k_h = 0.88 \text{ N m}^{-1}}$$

b. The maximum velocity is determined by taking the first derivative of Eq. 11.6.

$$y = A \sin(\omega\tau + \delta)$$

$$v_{\max} = \frac{dy}{d\tau} = \omega A \cos(\omega\tau + \delta)$$

Since  $|\cos \theta| \leq 1$  for all angles, it follows that the maximum velocity is,

$$v_{\max} = \omega A$$

Substituting  $\omega$  for Eq. 11.14 we can finally solve.

$$v_{\max} = \sqrt{\frac{k_h}{m}} A$$

$$v_{\max} = \sqrt{\frac{0.877\,298\,169\,\cancel{\text{kg}}\,\text{s}^{-2}}{0.2\,\cancel{\text{kg}}}} (0.010\,\text{m})$$

$$v_{\max} = 0.020\,943\,951\,\text{m s}^{-1}$$

$$\boxed{v_{\max} = 2.1 \times 10^{-2}\,\text{m s}^{-1}}$$

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**\*11.6.** If the average energy associated with a standing wave of frequency  $\nu$  in a cavity is

$$\bar{\varepsilon} = \frac{h\nu}{\exp(h\nu/k_{\text{B}}T) - 1}$$

deduce the expression for the low-frequency limit of the average energy associated with the standing wave.

**Solution:**

Given: expression above

Required: expression for the standing wave

The low-frequency limit can be obtained by use of the series expansion

$$e^x = 1 + x + \frac{x^2}{2!} + \dots$$

When  $x$  is small, we can make the approximation  $e^x = 1 + x$ , where  $x = \frac{h\nu}{k_{\text{B}}T}$ .

Thus, when  $h\nu \ll k_{\text{B}}T$ ,

$$\bar{\varepsilon} = \frac{h\nu}{1 + \frac{h\nu}{k_{\text{B}}T} - 1} = k_{\text{B}}T$$

Electromagnetic waves are transverse waves having two degrees of freedom. The value  $k_{\text{B}}T$  is divided between the two degrees of freedom.

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**11.7.** A sodium lamp of 50-watt power emits yellow light at 550 nm. How many photons does it emit each second? What is the momentum of each photon?

**Solution:**

Given:  $P = 50 \text{ W}$ ,  $\lambda = 550 \text{ nm}$

Required:  $E / \text{s}$ ,  $p$

We first determine the energy emitted in each photon using  $E = h\nu$ . The frequency is calculated from Eq. 11.1

$$\lambda \nu = c$$

$$\nu = \frac{c}{\lambda}$$

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{550 \times 10^{-9} \text{ m}}$$

$$E = 3.611\,772\,36 \times 10^{-19} \text{ J}$$

Recall that  $1 \text{ W} = 1 \text{ J s}^{-1}$ , therefore we can determine the number of photons emitted each second by dividing power by energy of a photon.

$$E / \text{s} = \frac{P}{E}$$

$$E / \text{s} = \frac{50 \text{ J s}^{-1}}{3.611\,772\,36 \times 10^{-19} \text{ J}}$$

$$E / \text{s} = 1.384\,361\,886 \times 10^{20} \text{ s}^{-1}$$

$$\boxed{E / \text{s} = 1.4 \times 10^{20} \text{ s}^{-1}}$$

The momentum is given by Eq. 11. 55

$$\lambda = \frac{h}{p}$$

$$p = \frac{6.626 \times 10^{-34} \text{ J s}}{550 \times 10^{-9} \text{ m}}$$

$$p = 1.204\,727\,27 \times 10^{-27} \text{ kg m s}^{-1}$$

$$\boxed{p = 1.20 \times 10^{-27} \text{ kg m s}^{-1}}$$

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**11.8.** The threshold frequency  $\nu_0$  for emission of photoelectrons from metallic sodium was found by Millikan, *Phys. Rev.*, 7, 1916, p. 362, to be  $43.9 \times 10^{13} \text{ s}^{-1}$ . Calculate the work function for sodium. A more recent value, for a carefully outgassed sample of sodium, is  $5.5 \times 10^{13} \text{ s}^{-1}$ . What work function corresponds to that value?

**Solution:**

Given:  $\nu = 43.9 \times 10^{13} \text{ s}^{-1}$ ,  $\nu_{\text{recent}} = 5.5 \times 10^{13} \text{ s}^{-1}$

Required:  $w$

The work function,  $w$ , is given in Eq. 11.37,

$$h\nu = \frac{1}{2}mu^2 + w$$

When the kinetic energy,  $\frac{1}{2}mu^2$  is zero, we get the expression  $h\nu_0 = w$ , with  $\nu_0$  as the threshold frequency. Solving for  $w$  we get,

$$w = h\nu_0$$

$$w = (6.626 \times 10^{-34} \text{ J s}) (43.9 \times 10^{13} \text{ s}^{-1})$$

$$w = 2.908814 \times 10^{-19} \text{ J}$$

$$\boxed{w = 2.91 \times 10^{-19} \text{ J}}$$

In eV, work is given as,

$$w = \frac{2.908814 \times 10^{-19} \text{ J}}{1.602 \times 10^{-19} \text{ J eV}^{-1}}$$

$$w = 1.815739076 \text{ eV}$$

$$\boxed{w = 1.82 \text{ eV}}$$

For the more recently determined value the work is,

$$w = (6.626 \times 10^{-34} \text{ J s}) (5.5 \times 10^{13} \text{ s}^{-1})$$

$$w = 3.6443 \times 10^{-20} \text{ J}$$

$$w = 3.6 \times 10^{-20} \text{ J}$$

$$w = \frac{3.6443 \times 10^{-20} \text{ J}}{1.602 \times 10^{-19} \text{ J eV}^{-1}}$$

$$w = 0.2274843945 \text{ eV}$$

$$w = 0.23 \text{ eV}$$

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**11.9.** Calculate the value of the de Broglie wavelength associated with

- a. an electron moving with a speed of  $6.0 \times 10^7 \text{ m s}^{-1}$  (this is the approximate velocity produced by a potential difference of 10 kV).
- b. an oxygen molecule moving with a speed of  $425 \text{ m s}^{-1}$  at  $0^\circ\text{C}$ .
- c. an  $\alpha$ -particle emitted by the disintegration of radium, moving at a speed of  $1.5 \times 10^7 \text{ m s}^{-1}$ .
- d. an electron having a speed of  $2.818 \times 10^8 \text{ m s}^{-1}$ .

**Solution:**

Given: see above

Required:  $\lambda_{\text{de Broglie}}$

The de Broglie wavelength is given by Eq. 11. 56,

$$\lambda = \frac{h}{p} = \frac{h}{mu}$$

- a. The mass of an electron is  $m = 9.11 \times 10^{-31} \text{ kg}$ , therefore

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.11 \times 10^{-31} \text{ kg})(6.0 \times 10^7 \text{ m s}^{-1})}$$

$$\lambda = 1.212\,221 \times 10^{-11} \text{ m}$$

$$\boxed{\lambda = 1.2 \times 10^{-11} \text{ m} = 12 \text{ pm}}$$

- b. The mass of  $\text{O}_2$  is obtained from its molar mass divided by the number of molecules per mole (Avogadro's constant).

$$M_{\text{O}_2} = 2 \times 15.9994 \text{ g mol}^{-1}$$

$$M_{\text{O}_2} = 31.9988 \text{ g mol}^{-1}$$

$$m_{\text{O}_2} = \frac{31.9988 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{\left( \frac{31.9988 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \right) (425 \text{ m s}^{-1})}$$

$$\lambda = 2.934\,063\,85 \times 10^{-11} \text{ m}$$

$$\boxed{\lambda = 2.93 \times 10^{-11} \text{ m} = 29.3 \text{ pm}}$$

- c. An alpha particle consists of two protons and two neutrons and can be written as  $\text{He}^{2+}$ . Hence, its molar mass is  $4 \text{ g mol}^{-1}$ . We can then solve in a similar manner as part b.

$$m_{\alpha} = \frac{4 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{\left( \frac{4 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \right) (1.5 \times 10^7 \text{ m s}^{-1})}$$

$$\lambda = 6.650\,295\,33 \times 10^{-15} \text{ m}$$

$$\boxed{\lambda = 6.7 \times 10^{-15} \text{ m} = 6.7 \text{ fm}}$$

- d. The mass of an electron is  $m = 9.11 \times 10^{-31} \text{ kg}$ , therefore

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.11 \times 10^{-31} \text{ kg})(2.818 \times 10^8 \text{ m s}^{-1})}$$

$$\lambda = 2.581\,024\,14 \times 10^{-12} \text{ m}$$

$$\boxed{\lambda = 2.58 \times 10^{-12} \text{ m} = 2.58 \text{ pm}}$$

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**11.10.** Consider a colloidal particle with a mass of  $6 \times 10^{-16}$  kg. Suppose that its position is measured to within 1.0 nm, which is about the resolving power of an electron microscope. Calculate the uncertainty in the velocity and comment on the significance of the result.

**Solution:**

Given:  $m = 6 \times 10^{-16}$  kg,  $\Delta q = 1.0$  nm

Required:  $\Delta u$ , comment on the result

The uncertainty of the velocity is given in Eq. 11.61

$$\Delta q \Delta u \geq \frac{\hbar}{2m}$$

Since  $\hbar = \frac{h}{2\pi}$ , we can substitute and solve for  $\Delta u$ .

$$\Delta q \Delta u \approx \frac{h}{4\pi m}$$

$$\Delta u = \frac{h}{4\pi m \Delta q}$$

$$\Delta u = \frac{(6.626 \times 10^{-34} \text{ J s} = \text{kg m}^2 \text{ s}^{-1})}{4\pi (6 \times 10^{-16} \text{ kg})(10^{-9} \text{ m})}$$

$$\Delta u = 8.788\,005\,44 \times 10^{-11} \text{ m s}^{-1}$$

$$\boxed{\Delta u = 9 \times 10^{-11} \text{ m s}^{-1}}$$

With this uncertainty in velocity, the position of the particle one second later would be uncertain to  $2 \times 9 \times 10^{-11} \text{ m s}^{-1}$  or 0.18 nm. This is only 0.18% of the diameter of the particle, and the uncertainty principle therefore does not present a serious problem for particles of this magnitude. For particles of molecular sizes, the uncertainty is much greater.

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**11.11.** Calculate the velocity and the de Broglie wavelength of an electron accelerated by a potential of

- a. 10 V,
- b. 1 kV, and
- c. 1 MV.

**Solution:**

Given: potentials above

Required:  $u$ ,  $\lambda_{\text{de Broglie}}$

To solve this problem, we use the procedure given in Example 11.2.

When a charge,  $q$ , is placed in an electric potential field,  $V$ , it experiences a force depending upon its position and starts to accelerate and pick up kinetic energy. This is given by  $E_k = qV$ .

- a. For a potential of 10 V,

$$E_k = eV$$

$$E_k = (1.602 \times 10^{-19} \text{ C})(10 \text{ V})$$

$$E_k = 1.602 \times 10^{-18} \text{ J}$$

The kinetic energy is  $\frac{1}{2}mu^2$  and therefore

$$u = \sqrt{\frac{2 \times 1.602 \times 10^{-18} \text{ J}}{9.11 \times 10^{-31} \text{ kg}}}$$

$$u = 1\,875\,370.435 \text{ m s}^{-1}$$

$$\boxed{u = 1.9 \times 10^6 \text{ m s}^{-1}}$$

From Eq. 11.56, the de Broglie wavelength  $\lambda$  is,

$$\lambda = \frac{h}{p} = \frac{h}{mu}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.11 \times 10^{-31} \text{ kg})(1875370.435 \text{ m s}^{-1})}$$

$$\lambda = 3.87834098 \times 10^{-10} \text{ m}$$

$$\boxed{\lambda = 3.9 \times 10^{-10} \text{ m} = 3.9 \times 10^2 \text{ pm}}$$

b. Using the same procedure above, we obtain,

$$E_k = (1.602 \times 10^{-19} \text{ C})(1000 \text{ V})$$

$$E_k = 1.602 \times 10^{-16} \text{ J}$$

$$u = \sqrt{\frac{2 \times 1.602 \times 10^{-16} \text{ J}}{9.11 \times 10^{-31} \text{ kg}}}$$

$$u = 18753704.35 \text{ m s}^{-1}$$

$$\boxed{u = 1.9 \times 10^7 \text{ m s}^{-1}}$$

The de Broglie wavelength  $\lambda$  is therefore,

$$\lambda = \frac{h}{mu}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.11 \times 10^{-31} \text{ kg})(18753704.35 \text{ m s}^{-1})}$$

$$\lambda = 3.87834098 \times 10^{-11} \text{ m}$$

$$\boxed{\lambda = 3.9 \times 10^{-11} \text{ m} = 3.9 \times 10 \text{ pm}}$$

c. Using the same procedure above, we obtain,

$$E_k = (1.602 \times 10^{-19} \text{ C})(10^6 \text{ V})$$

$$E_k = 1.602 \times 10^{-13} \text{ J}$$

$$u = \sqrt{\frac{2 \times 1.602 \times 10^{-13} \text{ J}}{9.11 \times 10^{-31} \text{ kg}}}$$

$$u = 593\,044\,203.2 \text{ m s}^{-1}$$

$$\boxed{u = 5.9 \times 10^8 \text{ m s}^{-1}}$$

The de Broglie wavelength  $\lambda$  is therefore,

$$\lambda = \frac{h}{mu}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.11 \times 10^{-31} \text{ kg})(593\,044\,203.2 \text{ m s}^{-1})}$$

$$\lambda = 1.226\,439\,1 \times 10^{-12} \text{ m}$$

$$\boxed{\lambda = 1.2 \times 10^{-12} \text{ m} = 1.2 \text{ pm}}$$

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**\*11.12.** The group velocity of a wave is given by the equation

$$v_g = \frac{dv}{d(1/\lambda)}$$

Prove that the group velocity of a de Broglie particle wave is equal to the ordinary velocity of the particle.

**Solution:**

Given: group velocity

Required: proof

From the expression  $E = h\nu$  and the definition of kinetic energy  $\frac{1}{2}mu^2$ , a particle of mass  $m$  has a frequency of,

$$\nu = \frac{E}{h}$$

$$\nu = \frac{mu^2}{2h}$$

Substituting the de Broglie wavelength, Eq. 11.56, into the newly acquired expression for frequency, we can eliminate the velocity term.

$$\lambda = \frac{h}{mu}$$

$$u = \frac{h}{m\lambda}$$

$$\nu = \frac{m}{2h} \left( \frac{h}{m\lambda} \right)^2$$

$$\nu = \frac{h}{2m\lambda^2}$$

The group velocity is therefore,

$$v_g = \frac{dv}{d(1/\lambda)}$$

$$v_g = \frac{d\left(\frac{h}{2m\lambda^2}\right)}{d(1/\lambda)}$$

$$v_g = 2\left(\frac{h}{2m}\right)\left(\frac{1}{\lambda}\right)$$

$$v_g = \frac{h}{m\lambda}$$

And from above,

$$\boxed{v_g = u}$$

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**11.13.** Photoelectric experiments show that about 5 eV of energy are required to remove an electron from platinum.

- What is the maximum wavelength of light that will remove an electron?
- If light of 150 nm wavelength were used, what is the velocity of the emitted electron?

**Solution:**

Given:  $E = 5 \text{ eV}$ , Pt

Required:  $\lambda_{\text{max}}$ ,  $u$

- The minimum frequency such that an electron can be removed from platinum is given by,

$$E = h\nu_{\text{min}}$$

$$\nu_{\text{min}} = \frac{E}{h}$$

And the corresponding maximum wavelength is therefore given by Eq. 11.1. Solving for  $\lambda_{\text{max}}$  we get,

$$\lambda\nu = c$$

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{ch}{E}$$

$$\lambda = \frac{(2.998 \times 10^8 \text{ m s}^{-1})(6.626 \times 10^{-34} \text{ J s})}{(5 \times 1.602 \times 10^{-19} \text{ J})}$$

$$\lambda = 2.479\,993\,508 \times 10^{-7} \text{ m}$$

$$\boxed{\lambda = 2.480 \times 10^{-7} \text{ m} = 248 \text{ nm}}$$

- The wavelength 150 nm corresponds to a frequency of

$$\lambda \nu = c$$

$$\nu = \frac{c}{\lambda}$$

$$\nu = \frac{(2.998 \times 10^8 \text{ m s}^{-1})}{(150 \times 10^{-9} \text{ m})}$$

$$\nu = 1.998\,666\,667 \times 10^{15} \text{ s}^{-1}$$

And to an energy of

$$E = (6.626 \times 10^{-34} \text{ J s}) (1.998\,666\,667 \times 10^{15} \text{ s}^{-1})$$

$$E = 1.324\,316\,53 \times 10^{-18} \text{ J}$$

The excess energy is therefore the difference between this value and the energy required to remove an electron from platinum.

$$E_{\text{excess}} = 1.324\,316\,53 \times 10^{-18} \text{ J} - (5 \times 1.602 \times 10^{-19} \text{ J})$$

$$E_{\text{excess}} = 5.233\,165\,33 \times 10^{-19} \text{ J}$$

The kinetic energy is  $\frac{1}{2}mu^2$  and therefore

$$u = \sqrt{\frac{2 \times 5.233\,165\,33 \times 10^{-19} \text{ J}}{9.11 \times 10^{-31} \text{ kg}}}$$

$$u = 1\,071\,859.934 \text{ m s}^{-1}$$

$$\boxed{u = 1.072 \times 10^6 \text{ m s}^{-1}}$$

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**11.14.** Calculate the kinetic energy of an electron that has a wavelength of (a) 10 nm, (b) 100 nm.

**Solution:**

Given:  $\lambda = 10 \text{ nm}$ ,  $\lambda = 100 \text{ nm}$

Required:  $E_k$

From the de Broglie equation, Eq. 11.56,  $\lambda = \frac{h}{p}$  and therefore

$$p = \frac{h}{\lambda}.$$

The kinetic energy  $E_k$  is given by

$$E_k = \frac{p^2}{2m}$$

Therefore,

$$E_k = \frac{h^2}{2m\lambda^2}$$

a. Solving for the kinetic energy where  $\lambda = 10 \text{ nm}$  gives,

$$E_k = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{2(9.11 \times 10^{-31} \text{ kg})(10 \times 10^{-9} \text{ m})^2}$$

$$E_k = 2.409\,652\,91 \times 10^{-21} \text{ J}$$

$$\boxed{E_k = 2.4 \times 10^{-21} \text{ J}}$$

b. Solving for the kinetic energy where  $\lambda = 100 \text{ nm}$  gives,



$$E_k = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{2(9.11 \times 10^{-31} \text{ kg})(100 \times 10^{-9} \text{ m})^2}$$

$$E_k = 2.409\,652\,91 \times 10^{-23} \text{ J}$$

$$\boxed{E_k = 2.4 \times 10^{-23} \text{ J}}$$

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**11.15.** Calculate the de Broglie wavelength of (a) an  $\alpha$ -particle (a helium nucleus) accelerated by a field of 100 V, and (b) a tennis ball served at 220 km h<sup>-1</sup>. (An  $\alpha$ -particle has a mass of  $6.64 \times 10^{-27}$  kg and a diameter of about  $10^{-15}$  m. A standard tennis ball has a mass of 55.4 g and a diameter of 6.51 cm.)

**Solution:**

Given: a.  $V_\alpha = 100$  V,  $m_\alpha = 6.64 \times 10^{-27}$  kg,  $d = 10^{-15}$  m

b.  $u_{\text{tennis ball}} = 220$  km h<sup>-1</sup>,  $m_{\text{tennis ball}} = 55.4$  g,  $d = 6.51$  cm

Required:  $\lambda_{\text{de Broglie}}$

d. For a potential of 100 V, the energy of an alpha particle is,

$$E_k = eV$$

$$E_k = (2 \times 1.602 \times 10^{-19} \text{ C})(100 \text{ V})$$

$$E_k = 3.204 \times 10^{-17} \text{ J}$$

The kinetic energy is  $\frac{1}{2}mu^2$  and therefore

$$u = \sqrt{\frac{2 \times 3.204 \times 10^{-17} \text{ J}}{6.64 \times 10^{-27} \text{ kg}}}$$

$$u = 98\,237.479 \text{ m s}^{-1}$$

The de Broglie wavelength  $\lambda$  is therefore,

$$\lambda = \frac{h}{mu}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(6.64 \times 10^{-27} \text{ kg})(98\,237.479 \text{ m s}^{-1})}$$

$$\lambda = 1.015\,795\,16 \times 10^{-12} \text{ m}$$

$$\boxed{\lambda = 1.02 \times 10^{-12} \text{ m}}$$

Thus the wavelength is about 1000 times larger than the diameter of the particle.

e. We convert the velocity of the tennis ball to  $\text{m s}^{-1}$  and then determine the wavelength.

$$u = 220 \text{ km h}^{-1} \times \frac{10^3 \text{ m}}{\text{km}} \times \frac{\text{h}}{3600 \text{ s}}$$

$$u = 61.11111111 \text{ m s}^{-1}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(55.4 \times 10^{-3} \text{ kg})(61.11111111 \text{ m s}^{-1})}$$

$$\lambda = 1.95713817 \times 10^{-34} \text{ m}$$

$$\boxed{\lambda = 1.96 \times 10^{-34} \text{ m}}$$

This is about  $3 \times 10^{32}$  times smaller than the diameter of the tennis ball.

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**11.16.** Assume that the three real functions  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  are normalized and orthogonal. Normalize the following functions:

a.  $\psi_1 + \psi_2$

b.  $\psi_1 - \psi_2$

c.  $\psi_1 + \psi_2 + \psi_3$

d.  $\psi_1 - \frac{1}{\sqrt{2}}\psi_2 + \frac{\sqrt{3}}{\sqrt{2}}\psi_3$

**Solution:**

Given: three real functions  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  ; all normalized and orthogonal

Required: Normalize a – d

a. The normalization condition for any function  $\psi$  is given by Eq. 11. 89 as,

$$\int \psi^* \psi d\tau = 1$$

In other words, to normalize the function  $\psi_1 + \psi_2$ , we multiply by its conjugate and set its integral equal to 1. Since we are told that all three functions are real, the conjugate of  $\psi_1 + \psi_2$  is simply  $\psi_1 + \psi_2$ . When solving we introduce a factor  $N$ .

Reading sections titled *Normalization* and *Normalization Condition* will help further understand normalization.

$$\int N(\psi_1 + \psi_2)N(\psi_1 + \psi_2)d\tau = 1$$

$$N^2 \int (\psi_1 + \psi_2)^2 d\tau = 1$$

$$N^2 \left[ \int \psi_1^2 d\tau + 2 \int \psi_1 \psi_2 d\tau + \int \psi_2^2 d\tau \right] = 1$$

The first and last integrals are equal to unity since  $\psi_1$  and  $\psi_2$  are normalized, as given in the problem. The second integral is equal to zero ( $2 \int \psi_1 \psi_2 d\tau = 0$ ) since the wave function is orthogonal. Eq. 11.111 defines orthogonality as,

$$\int \psi_1^* \psi_2 d\tau = 0$$

This leads to the result,

$$N^2[1+0+1]=1$$

$$2N^2=1$$

$$N = \frac{1}{\sqrt{2}}$$

The normalized wave function is therefore,

$$\boxed{\frac{1}{\sqrt{2}}(\psi_1 + \psi_2)}$$

b. We apply the same rationale as above to solve for the normalized wave functions in the following cases.

$$N^2 \int (\psi_1 - \psi_2)^2 d\tau = 1$$

$$N^2 \left[ \int \psi_1^2 d\tau - 2 \int \psi_1 \psi_2 d\tau + \int \psi_2^2 d\tau \right] = 1$$

$$N^2[1-0+1]=1$$

$$2N^2=1$$

$$N = \frac{1}{\sqrt{2}}$$

$$\boxed{\frac{1}{\sqrt{2}}(\psi_1 - \psi_2)}$$

c.

$$N^2 \int (\psi_1 + \psi_2 + \psi_3)^2 d\tau = 1$$

$$N^2 \left[ \int \psi_1^2 d\tau + \int \psi_2^2 d\tau + \int \psi_3^2 d\tau + 2 \int \psi_1 \psi_2 d\tau + 2 \int \psi_1 \psi_3 d\tau + 2 \int \psi_2 \psi_3 d\tau \right] = 1$$

$$N^2 [1+1+1+0+0+0] = 1$$

$$3N^2 = 1$$

$$N = \frac{1}{\sqrt{3}}$$

$$\boxed{\frac{1}{\sqrt{3}}(\psi_1 + \psi_2 + \psi_3)}$$

d.

$$N^2 \int \left( \psi_1 - \frac{1}{\sqrt{2}}\psi_2 + \frac{\sqrt{3}}{\sqrt{2}}\psi_3 \right)^2 d\tau = 1$$

$$N^2 \left[ \int \psi_1^2 d\tau + \frac{1}{2} \int \psi_2^2 d\tau + \frac{3}{2} \int \psi_3^2 d\tau - \frac{2}{\sqrt{2}} \int \psi_1 \psi_2 d\tau - \frac{2\sqrt{3}}{\sqrt{2}} \int \psi_1 \psi_3 d\tau - \frac{2\sqrt{3}}{\sqrt{2}} \int \psi_2 \psi_3 d\tau \right] = 1$$

$$N^2 [1+1+1+0+0+0] = 1$$

$$3N^2 = 1$$

$$N = \frac{1}{\sqrt{3}}$$

$$\frac{1}{\sqrt{3}} \left( \psi_1 - \frac{1}{\sqrt{2}}\psi_2 + \frac{\sqrt{3}}{\sqrt{2}}\psi_3 \right)$$

$$\boxed{\left( \frac{1}{\sqrt{3}}\psi_1 - \frac{1}{\sqrt{6}}\psi_2 + \frac{1}{\sqrt{2}}\psi_3 \right)}$$

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**11.17.** Is the function  $Ae^{-ax}$  an eigenfunction of the operator  $d^2/dx^2$ ? If so, what is the eigenvalue?

**Solution:**

Given:  $Ae^{-ax}$

Required: answer the question, find eigenvalue if applicable

If  $Ae^{-ax}$  is an eigenfunction of  $d^2/dx^2$ , an operation on  $Ae^{-ax}$  twice by  $d/dx$  will give the original function multiplied by a constant.

$$\frac{d}{dx}(Ae^{-ax}) = -Aae^{-ax}$$

$$\frac{d}{dx}(-Aae^{-ax}) = Aa^2e^{-ax}$$

Since the operation returns the original function multiplied by a constant,  $a^2$ , then  $Ae^{-ax}$  is an eigenfunction of the operator  $d^2/dx^2$  with eigenvalue  $a^2$ .

eigenvalue = $a^2$
--------------------

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**11.18.** Prove that  $m_l$  must be integral in order for the function

$$\Phi = \sin m_l \phi$$

to be an acceptable wave function.

**Solution:**

Given: function above

Required: proof

For the wave function to be single valued,

$$\Phi = \sin m_l \phi \text{ must equal } \Phi = \sin(m_l(\phi + 2\pi))$$

Using the double angle formulas, we obtain the expression for  $\Phi = \sin(m_l(\phi + 2\pi))$  as,

$$\Phi = \sin(m_l \phi + 2\pi m_l)$$

$$\sin(A + B) = \sin A \cos B + \sin B \cos A$$

$$\Phi = \sin m_l \phi \cos 2\pi m_l + \sin 2\pi m_l \cos m_l \phi$$

For this to equal  $\sin m_l \phi$ ,  $\cos 2\pi m_l$  must be 1 and therefore  $2\pi m_l = 0$ . This is only true if  $m_l$  is an integer value.

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**11.19.** The energy operator for a time-dependent system (Table 11.1) is

$$i\hbar \frac{\partial}{\partial t}$$

A possible eigenfunction for the system is

$$\Psi(x, y, z, t) = \psi(x, y, z) \exp(-2\pi i E t / \hbar)$$

Show that  $\Psi^* \Psi$ , the probability density, is independent of time.

**Solution:**

Given: energy operator,  $\Psi(x, y, z, t)$

Required: Show that  $\Psi^* \Psi$ , the probability density, is independent of time.

First of all, we do not consider the energy operator to solve this problem.

We are given eigenfunction,

$$\Psi(x, y, z, t) = \psi(x, y, z) e^{-2\pi i E t / \hbar}$$

Its conjugate is given by,

$$\Psi^*(x, y, z, t) = \psi^*(x, y, z) e^{2\pi i E t / \hbar}$$

The probability density is therefore,

$$\Psi^* \Psi = \psi^* e^{-2\pi i E t / \hbar} \psi e^{2\pi i E t / \hbar}$$

$$\Psi^* \Psi = \psi^* \psi e^0$$

$$\Psi^* \Psi = \psi^* \psi$$

The exponential term, containing the time dependence is cancelled out, leaving only the  $\psi$  functions which is simply a function of  $x, y$  and  $z$ . Therefore the probability density is independent of time.

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**\*11.20.** Prove that the momentum operator corresponding to  $p_x$  is a Hermitian operator.

**Solution:**

Given:  $p_x$

Required: proof

The momentum operator  $p_x$  is given in Table 11.1 as,

$$-i\hbar \frac{\partial}{\partial x}$$

The definition for a Hermitian operator is given by Eq. 11.106,

$$\int \psi_2^* \hat{F} \psi_1 d\tau = \int \psi_1 (\hat{F} \psi_2)^* d\tau$$

Where  $\hat{F}$  is an operator and  $\psi_1$  and  $\psi_2$  are any two functions.

Using the momentum operator and the functions  $\psi(x)$  and  $\phi(x)$  for clarity we must prove that,

$$\int \phi^* \left( -i\hbar \frac{\partial \psi}{\partial x} \right) dx = \int \psi \left( -i\hbar \frac{\partial \phi}{\partial x} \right)^* dx$$

Using integration by parts on the left side gives,

$$\int \phi^* \left( -i\hbar \frac{\partial \psi}{\partial x} \right) dx = -i\hbar [\phi^* \psi]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi \left( -i\hbar \frac{\partial \phi^*}{\partial x} \right) dx$$

The first term is zero since all wave functions must asymptotically go to zero at  $\pm\infty$ . The second term is

$$\begin{aligned} &= 0 - \int_{-\infty}^{\infty} \psi \left( -i\hbar \frac{\partial \phi^*}{\partial x} \right) dx \\ &= \int_{-\infty}^{\infty} \psi \left( -i\hbar \frac{\partial \phi^*}{\partial x} \right) dx \end{aligned}$$

Which is the same as the right hand side as the equation given above. Therefore operator is Hermitian.

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**11.21.** Which of the following functions is an eigenfunction of the operator  $d/dx$ ?

- |              |                 |
|--------------|-----------------|
| a. $k$       | d. $\exp(kx)$   |
| b. $kx^2$    | e. $\exp(kx^2)$ |
| c. $\sin kx$ | f. $\exp(ikx)$  |

( $k$  is a constant, and  $i$  is the square root of minus one.) Give the eigenvalue where appropriate.

**Solution:**

Given: a – d

Required: eigenfunction of  $d/dx$ , eigenvalues

As stated in problem 11.17, if the operation returns the original function multiplied by a constant, the function is an eigenfunction.

a.  $\frac{dk}{dx} = 0 = 0(k)$

Therefore  $k$  is an eigenfunction of the operator  $d/dx$  with eigenvalue = 0

b.  $\frac{dkx^2}{dx} = 2kx$

$kx^2$  is not an eigenfunction of the operator  $d/dx$ .

c.  $\frac{d \sin kx}{dx} = k \cos kx$

$\sin kx$  is not an eigenfunction of the operator  $d/dx$ .

d.  $\frac{de^{kx}}{dx} = ke^{kx}$

$e^{kx}$  is an eigenfunction of the operator  $d/dx$  with eigenvalue =  $k$

e.  $\frac{de^{kx^2}}{dx} = 2kxe^{kx^2}$

$e^{kx^2}$  is not an eigenfunction of the operator  $d/dx$ .

f.  $\frac{de^{ikx}}{dx} = ike^{ikx}$

$e^{ikx}$  is an eigenfunction of the operator  $d/dx$  with eigenvalue =  $ik$

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**11.22.** Figure 11.20 shows the angular momentum vectors for  $l = 2$  and for  $m = 2, 1, 0, -1, -2$ . In each case, calculate the angles the vectors make with the  $Z$  axis.

**Solution:**

Given: Figure 11.20

Required:  $\theta$

From the figure, we see that the length  $L$  of each vector is given by

$$L = \sqrt{2(2+1)}\hbar$$

$$L = \sqrt{6}\hbar$$

The  $Z$  component in each case is given by

$$m_l\hbar$$

Using trigonometry, we see that the cosine of each angle is therefore  $\cos \theta = \frac{m_l}{\sqrt{6}}$ .

Solving for the case where  $m_l = 2$ ,

$$\theta = \cos^{-1}\left(\frac{2}{\sqrt{6}}\right)$$

$$\theta = 35.264\,389\,68$$

$$\boxed{\theta = 35.3}$$

Using the procedure as above, we obtain the following results.

$m_l$	2	1	0	-1	-2
$\theta / \text{deg}$	35.3	65.9	90.0	114.1	144.7

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**11.23.** Show that the one-electron wave functions  $\psi_{nlm}$  are also eigenfunctions of the operator  $(\hat{L}_x^2 + \hat{L}_y^2)$ . What physical property (observable) is associated with this operator?

**Solution:**

Given:  $\psi_{nlm}$  and  $(\hat{L}_x^2 + \hat{L}_y^2)$ .

Required: proof

From Eq. 11. 203 we are given that

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Therefore, by rearranging we get

$$\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}^2 - \hat{L}_z^2$$

To show that the one-electron wave functions  $\psi_{nlm}$  are also eigenfunctions of this operator, we perform the following,

$$(\hat{L}_x^2 + \hat{L}_y^2) \psi_{nlm} = (\hat{L}^2 - \hat{L}_z^2) \psi_{nlm}$$

Then from Eq. 11. 208 and Eq. 11.211, we substitute the eigenvalues below

$$= (l(l+1)\hbar^2 - m_l^2\hbar^2) \psi_{nlm}$$

$$= (l(l+1) - m_l^2) \hbar^2 \psi_{nlm}$$

Therefore  $\psi_{nlm}$  are eigenfunctions of the operator  $\hat{L}_x^2 + \hat{L}_y^2$  with eigenvalues  $(l(l+1) - m_l^2) \hbar^2$ .

The operator  $\hat{L}_x^2 + \hat{L}_y^2$  corresponds to  $x^2 + y^2$  and the equation,

$$x^2 + y^2 = a^2,$$

Which is the equation for a circle with radius  $a$ . The physical property corresponding to the operator is thus the square of the radius of the base of the angular momentum vector as it rotates about the Z axis. (see Figure 11.20)

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**11.24.** Explain why the Heisenberg uncertainty principle would be violated if the harmonic oscillator ground-state energy were zero.

**Solution:**

Given: situation above

Required: explain

If the harmonic oscillator ground state energy were zero, the implications is that the kinetic and potential energies are both zero (since neither can take on negative values). Therefore the momentum is exactly zero. Also, from the nature of the potential-energy function, the total energy can only be zero at  $x = 0$ . Therefore, this leads to a situation where we know the values of the momentum and position simultaneously and exactly. This is a violation of the Uncertainty Principle.

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**11.25.** Calculate the lowest possible energy for an electron confined in a cube of sides equal to

- a. 10 pm and
- b. 1 fm (1 femtometre =  $10^{-15}$  m).

The latter cube is the order of magnitude of an atomic nucleus; what do you conclude from the energy you calculate about the probability of a free electron being present in a nucleus?

**Solution:**

Given: electron in a box,  $a = 10$  pm,  $a = 1$  fm

Required:  $E$

From Eq. 11.151 the expression for the energy of a particle in a box is given by

$$E = \frac{h^2}{8ma^2} (n_1^2 + n_2^2 + n_3^2)$$

For the lowest energy possible we set  $n_1 = n_2 = n_3 = 1$ . Using  $m$  as the mass of an electron, we solve for  $E$  in each case.

$$E = \frac{3(6.626 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})a^2}$$

a.

$$a = 10 \times 10^{-12} \text{ m}$$

$$a = 1.0 \times 10^{-11} \text{ m}$$

$$E = \frac{3(6.626 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^{-11} \text{ m})^2}$$

$$E = 1.807\,239\,68 \times 10^{-15} \text{ J}$$

$$\boxed{E = 1.8 \times 10^{-15} \text{ J}}$$

In eV,

$$E = \frac{1.807\,239\,68 \times 10^{-15} \text{ J}}{1.602 \times 10^{-19} \text{ eV}^{-1}}$$

$$E = 11\,281.146\,58 \text{ eV}$$

$$\boxed{E = 1.1 \times 10^4 \text{ eV}}$$

b.

$$a = 1 \times 10^{-15} \text{ m}$$

$$E = \frac{3(6.626 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})(1 \times 10^{-15} \text{ m})^2}$$

$$E = 1.807\,239\,682 \times 10^{-7} \text{ J}$$

$$\boxed{E = 1.81 \times 10^{-7} \text{ J}}$$

$$E = \frac{1.807\,239\,682 \times 10^{-7} \text{ J}}{1.602 \times 10^{-19} \text{ eV}^{-1}}$$

$$E = 1.128\,114\,658 \times 10^{12} \text{ eV}$$

$$\boxed{E = 1.13 \times 10^{12} \text{ eV}}$$

The latter energy is so large that one electron would not remain in the nucleus, but would be emitted as a  $\beta$  particle.

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**11.26.** A particle is moving in one dimension between  $x = a$  and  $x = b$ . The potential energy is such that the particle cannot be outside these limits and that the wave function in between is

$$\psi = A/x$$

- a. Determine the normalization constant  $A$ .
- b. Calculate the average value of  $x$ .

**Solution:**

Given:  $x = a, x = b, \psi = A/x$

Required:  $A, \langle x \rangle$

a. The normalization condition is given by Eq. 11.89

$$\int \psi^* \psi d\tau = 1$$

For this wave function, the normalization condition becomes,

$$\int_a^b \psi^* \psi dx = 1$$

Solving for  $A$  we obtain,

$$\int_a^b (A/x)(A/x) dx = 1$$

$$\int_a^b \frac{A^2}{x^2} dx = 1$$

$$A^2 \left[ -\frac{1}{x} \right]_a^b = 1$$

$$A^2 \left[ -\frac{1}{a} + \frac{1}{b} \right] = 1$$

$$A^2 \left[ \frac{b-a}{ab} \right] = 1$$

$$A^2 = \frac{ab}{b-a}$$

$$A = \sqrt{\frac{ab}{b-a}}$$

b. To find the average value of  $x$  we use Eq.11.104

$$\overline{F} \equiv \langle F \rangle = \frac{\int_{-\infty}^{\infty} \psi^* (\hat{F} \psi) d\tau}{\int_{-\infty}^{\infty} \psi^* \psi d\tau}$$

Since we have normalized the function,  $\psi = \sqrt{\frac{ab}{b-a}} \left( \frac{1}{x} \right)$ , the denominator becomes 1 and we can solve as,

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* (x\psi) dx$$

$$\langle x \rangle = \int_a^b \sqrt{\frac{ab}{b-a}} \left( \frac{1}{x} \right) \sqrt{\frac{ab}{b-a}} \left( \frac{1}{x} \right) dx$$

$$\langle x \rangle = \frac{ab}{b-a} \int_a^b \frac{1}{x} dx$$

$$\langle x \rangle = \frac{ab}{b-a} [\ln x]_a^b$$

$$\boxed{\langle x \rangle = \frac{ab}{b-a} \ln \frac{b}{a}}$$

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**11.27.** An electron is confined in a one-dimensional box 1 nm long. How many energy levels are there with energy less than 10 eV? How many levels are there with energy between 10 and 100 eV?

**Solution:**

Given:  $a = 1 \text{ nm}$ ,  $E = 10 \text{ eV}$ ,  $E = 100 \text{ eV}$

Required:  $n$

To calculate the  $n$ th energy level, we use Eq. 11.149

$$E_n = \frac{n^2 (6.626 \times 10^{-34} \text{ J s})^2}{8 (9.11 \times 10^{-31} \text{ kg}) (1 \times 10^{-9} \text{ m})^2}$$

$$E_n = 6.02413227 \times 10^{-20} n^2 \text{ J}$$

$$E_n = \frac{6.02413227 \times 10^{-20} n^2 \text{ J}}{1.602 \times 10^{-19} \text{ J eV}^{-1}}$$

$$E_n = 0.3760382192 n^2 \text{ eV}$$

$$n = \sqrt{\frac{E_n}{0.3760382192 \text{ eV}}}$$

At 10 eV,

$$n = \sqrt{\frac{10 \text{ eV}}{0.3760382192 \text{ eV}}}$$

$$n = 5.15684415$$

$$\boxed{n \approx 5}$$

Thus, levels 1 through 5 have energies less than 10 eV.

At 100 eV,

$$n = \sqrt{\frac{100 \text{ eV}}{0.376 038 219 2 \text{ eV}}}$$

$$n = 16.307 373 05$$

$$\boxed{n \approx 16}$$

Thus, levels 6 through 16 have energies between 10 eV and 100 eV.

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**11.28.** Determine whether the eigenfunctions obtained in Section 11.6 for a particle in a one-dimensional box are eigenfunctions for the momentum operator. If they are, obtain the eigenvalues; if they are not, explain why.

**Solution:**

Given: Section 11.6

Required: determined if eigenfunctions, eigenvalues

The solution for a particle in a one-dimensional box is given by Eq. 11.148 as

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

The momentum operator  $p_x$  is given in Table 11.1 as,

$$-i\hbar \frac{\partial}{\partial x}$$

As stated in problem 11.17, if the operation returns the original function multiplied by a constant, the function is an eigenfunction.

$$\begin{aligned} &= -i\hbar \frac{\partial \psi_n}{\partial x} \\ &= -i\hbar \frac{\partial}{\partial x} \left( \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \right) \\ &= -i\hbar \sqrt{\frac{2}{a}} \frac{\partial}{\partial x} \left( \sin\left(\frac{n\pi x}{a}\right) \right) \\ &= -i\hbar \sqrt{\frac{2}{a}} \left( \frac{n\pi}{a} \right) \cos\left(\frac{n\pi x}{a}\right) \end{aligned}$$

Since the result is not a constant multiplied by  $\psi_n$ ,  $\psi_n$  is not an eigenfunction of the momentum operator. This conclusion is related to the Heisenberg uncertainty principle; the position and momentum operators do not commute, there are no common eigenfunctions, and the two properties cannot be measured simultaneously and precisely. However, the eigenfunction  $\psi_n$ , like any other function, can be expressed as a linear combination of the set of momentum eigenfunctions (compare Eq. 11.117 to Eq. 11.120). The physical significance of this is that



the function  $\psi_n$  corresponds to the wave train of particular momentum being reflected at the walls of the box and giving rise to a wave train in the opposite direction.

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**\*11.29.** Treat the three-dimensional particle in a box of sides  $a$ ,  $b$ , and  $c$  by analogy with the treatment in Section 11.6. Assume the potential to be zero inside the box and infinite outside, and proceed by the following steps:

- Write the basic differential equation that must be solved for the three-dimensional problem.
- Separate the equation from (a) into terms involving  $X(x)$ ,  $Y(y)$ , and  $Z(z)$ .
- Determine the expressions for  $X$ ,  $Y$ , and  $Z$ .
- Obtain the expression (Eq. 11.150) for the total energy.

**Solution:**

Given: three-dimensional particle in a box

Required: see above

- a. The basic differential equation that must be solved is a three-dimensional form of the Schrodinger, Eq. 11.86.

$$\hat{H}\psi = E\psi$$

From Table 11.1 we get,

$$-\frac{\hbar^2}{2m}\nabla^2\psi + E_p(x, y, z)\psi = E\psi$$

Notice that this is analogous to Eq. 11.85

- b. The potential energy,  $E_p$  can be set to zero inside the box, and using the definition for the Del-squared or Laplacian operator, Eq. 11.81, we get,

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi &= E\psi \\ \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} &= -\frac{2mE}{\hbar^2}\psi\end{aligned}$$

The energy,  $E$ , is separated into its component parts,

$$E = E_x + E_y + E_z$$

And the wave function is factored as,

$$\psi = X(x)Y(y)Z(z)$$

Substitution of the factored wave function gives,

$$\frac{\partial^2 XYZ}{\partial x^2} + \frac{\partial^2 XYZ}{\partial y^2} + \frac{\partial^2 XYZ}{\partial z^2} = \left( -\frac{2mE_x}{\hbar^2} - \frac{2mE_y}{\hbar^2} - \frac{2mE_z}{\hbar^2} \right) XYZ$$

Dividing by XYZ to eliminate the wave function from the right hand side of the equation gives,

$$\frac{1}{XYZ} \frac{\partial^2 XYZ}{\partial x^2} + \frac{1}{XYZ} \frac{\partial^2 XYZ}{\partial y^2} + \frac{1}{XYZ} \frac{\partial^2 XYZ}{\partial z^2} = -\frac{2mE_x}{\hbar^2} - \frac{2mE_y}{\hbar^2} - \frac{2mE_z}{\hbar^2}$$

c. Solving the first term we get

$$\frac{1}{XYZ} \frac{\partial^2 XYZ}{\partial x^2} = \frac{1}{XYZ} \frac{\partial}{\partial x} \left( \frac{\partial XYZ}{\partial x} \right)$$

$$\frac{1}{XYZ} \frac{\partial^2 XYZ}{\partial x^2} = \frac{1}{XYZ} \frac{\partial}{\partial x} \left( YZ \frac{\partial X}{\partial x} \right)$$

$$\frac{1}{XYZ} \frac{\partial^2 XYZ}{\partial x^2} = \frac{1}{XYZ} YZ \frac{\partial^2 X}{\partial x^2}$$

$$\frac{1}{XYZ} \frac{\partial^2 XYZ}{\partial x^2} = \frac{1}{X} \frac{\partial^2 X}{\partial x^2}$$

Therefore,

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} = -\frac{2mE_x}{\hbar^2}$$

Similarly, we get

$$\frac{1}{Y} \frac{\partial^2 Y}{\partial x^2} = -\frac{2mE_y}{\hbar^2}$$

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial x^2} = -\frac{2mE_z}{\hbar^2}$$

d. The total energy is given by Eq. 11.150 as

$$E = \frac{h^2}{8m} \left( \frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right)$$

This becomes

$$E = E_x + E_y + E_z = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

If  $a = b = c$ , then

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

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**11.30.** What is the quantum-mechanical probability of finding the particle in a one-dimensional “box” in the middle third of the “box”? Derive an expression that shows how this quantity depends on the quantum number  $n$ .

**Solution:**

Given: one-dimensional box

Required: probability

The quantum mechanical probability is given by

$$P = \int \psi^* \psi d\tau$$

Since we are trying to find the particle in the middle third of the box, we consider the region between the first third and the second third of the box. If the box is of length  $a$ , then we have the boundaries  $a/3$  and  $2a/3$ .

We use the wave function in the form of Eq. 11.148 to solve.

$$P = \int_{a/3}^{2a/3} \left( \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \right)^2 dx$$

$$P = \frac{2}{a} \int_{a/3}^{2a/3} \sin^2\left(\frac{n\pi x}{a}\right) dx$$

Using the fact that  $\sin^2 bx = \frac{1}{2}(1 - \cos 2bx)$ , we continue to solve.

$$P = \frac{2}{a} \int_{a/3}^{2a/3} \frac{1}{2} \left( 1 - \cos \left( \frac{2n\pi x}{a} \right) \right) dx$$

$$P = \frac{1}{a} \int_{a/3}^{2a/3} 1 - \cos \left( \frac{2n\pi x}{a} \right) dx$$

$$P = \frac{1}{a} \left[ x - \frac{a}{2n\pi} \sin \left( \frac{2n\pi x}{a} \right) \right]_{a/3}^{2a/3}$$

$$P = \frac{1}{a} \left[ \frac{2a}{3} - \frac{a}{3} - \frac{a}{2n\pi} \sin \left( \frac{4n\pi}{3} \right) + \frac{a}{2n\pi} \sin \left( \frac{2n\pi}{3} \right) \right]$$

$$P = \frac{1}{a} \left[ \frac{a}{3} - \frac{a}{2n\pi} \sin \left( \frac{4n\pi}{3} \right) + \frac{a}{2n\pi} \sin \left( \frac{2n\pi}{3} \right) \right]$$

$$P = \frac{1}{3} - \frac{1}{2n\pi} \left[ \sin \left( \frac{4n\pi}{3} \right) - \sin \left( \frac{2n\pi}{3} \right) \right]$$

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**11.31.** The classical probability for finding a particle in the region  $x$  to  $x + dx$  in a one-dimensional box of length  $a$  is  $dx/a$ .

- Derive the classical probability for finding the particle in the middle third of the box.
- Show that as  $n \rightarrow \infty$ , the quantum probability obtained in the previous problem becomes identical to the classical result.

**Solution:**

Given: box of length  $a$ ,  $P_{\text{one dimension}} = dx/a$

Required:  $P$ , proof

a. We use a similar approach as problem 11.30 to obtain the classical probability for finding the particle in the middle third of the box. Since the classical probability of finding a particle in the region  $x$  to  $x + dx$  in a one-dimensional box of length  $a$  is  $dx/a$ , then the probability for finding the particle in the middle third of the box is calculated from the integral between  $a/3$  and  $2a/3$ .

$$P_{\text{classical}} = \int_{a/3}^{2a/3} \frac{dx}{a}$$

$$P_{\text{classical}} = \frac{x}{a} \Big|_{a/3}^{2a/3}$$

$$P_{\text{classical}} = \frac{1}{a} \left( \frac{2a}{3} - \frac{a}{3} \right)$$

$$P_{\text{classical}} = \frac{1}{a} \left( \frac{a}{3} \right)$$

$$\boxed{P_{\text{classical}} = \frac{1}{3}}$$

b. The result obtained in the previous problem is

$$P = \frac{1}{3} - \frac{1}{2n\pi} \left[ \sin\left(\frac{4n\pi}{3}\right) - \sin\left(\frac{2n\pi}{3}\right) \right]$$

Since  $n$  can only be an integer, the quantity in the square brackets in the solution can only have three values.

$$\begin{aligned}\left[\sin\left(\frac{4n\pi}{3}\right) - \sin\left(\frac{2n\pi}{3}\right)\right] &= 0 && \text{if } n = 3, 6, 9 \dots \\ &= -\sqrt{3} && \text{if } n = 1, 4, 7 \dots \\ &= \sqrt{3} && \text{if } n = 2, 5, 8 \dots\end{aligned}$$

Therefore, we determine that as  $n \rightarrow \infty$ , the second term will vanish, since we multiply the square bracket by  $\frac{1}{2n\pi}$ . This yields a result identical to the classical probability above.

$$P_{\text{quantum}} = \frac{1}{3} - \cancel{\frac{1}{2n\pi}} \left[ \sin\left(\frac{4n\pi}{3}\right) - \sin\left(\frac{2n\pi}{3}\right) \right]$$

$$\boxed{P_{\text{quantum}} = P_{\text{classical}} = \frac{1}{3}}$$

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**\*11.32.** Problem 11.25 is concerned with the calculation of the minimum energy for an electron confined in a cube. Another approach to the problem is to consider, on the basis of the uncertainty principle (Eq. 11.60), the uncertainty in the energy if the uncertainty in the position is equal to the length of the side of the cube. Calculate  $\Delta E$  for a cube of sides equal to

- a. 10 pm and
- b. 1 fm ( $10^{-15}$  m),

and compare the results with the minimum energies found for Problem 11.25.

**Solution:**

Given: electron in a box,  $a = 10$  pm,  $a = 1$  fm, Eq. 11.60

Required:  $\Delta E$ , compare the results with the Problem 11.25

The uncertainty principle is given as Eq. 11.60,

$$\Delta q \Delta p \geq \frac{1}{2} \hbar$$

Since  $E = \frac{p^2}{2m}$  and  $\hbar = \frac{h}{2\pi}$ , we use rearrange Eq. 11.60 to obtain an expression for  $\Delta E$ .

$$\Delta p = \frac{1}{2\Delta q} \left( \frac{h}{2\pi} \right)$$

$$\Delta p = \frac{h}{4\pi\Delta q}$$

$$\Delta E = \left( \frac{h}{4\pi\Delta q} \right)^2 \frac{1}{2m}$$

$$\Delta E = \frac{h^2}{32\pi^2 m (\Delta q)^2}$$

c.

$$a = 10 \times 10^{-12} \text{ m}$$

$$a = 1.0 \times 10^{-11} \text{ m}$$

$$\Delta E = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{32\pi^2 (9.11 \times 10^{-31} \text{ kg}) (1.0 \times 10^{-11} \text{ m})^2}$$

$$\Delta E = 1.525\,930\,53 \times 10^{-17} \text{ J}$$

$$\boxed{E = 1.5 \times 10^{-17} \text{ J}}$$

In eV,

$$\Delta E = \frac{1.525\,930\,53 \times 10^{-17} \cancel{\text{J}}}{1.602 \times 10^{-19} \cancel{\text{J}} \text{ eV}^{-1}}$$

$$\Delta E = 95.251\,593\,67 \text{ eV}$$

$$\boxed{\Delta E = 95 \text{ eV}}$$

d.

$$a = 1 \times 10^{-15} \text{ m}$$

$$\Delta E = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{32\pi^2 (9.11 \times 10^{-31} \text{ kg}) (1 \times 10^{-15} \text{ m})^2}$$

$$\Delta E = 1.525\,930\,531 \times 10^{-9} \text{ J}$$

$$\boxed{\Delta E = 1.5 \times 10^{-9} \text{ J}}$$

$$\Delta E = \frac{1.525\,930\,531 \times 10^{-9} \cancel{\text{J}}}{1.602 \times 10^{-19} \cancel{\text{J}} \text{ eV}^{-1}}$$

$$\Delta E = 9\,525\,159\,367 \text{ eV}$$

$$\boxed{\Delta E = 9.5 \times 10^9 \text{ eV}}$$

These uncertainties are considerably smaller than the energies calculated for the particle in a box. If we compare the expression for  $E$  used in problem 11.25 to the one used for  $\Delta E$ , we find that they are smaller by a factor of,

$$\frac{E}{\Delta E} = \left( \frac{3h^2}{8ma^2} \right) \div \left( \frac{h^2}{32\pi^2 m (\Delta q)^2} \right)$$

$$\frac{E}{\Delta E} = \left( \frac{3\cancel{h^2}}{8\cancel{m} \cancel{a^2}} \right) \times \left( \frac{32\pi^2 \cancel{m} (\Delta q)^2}{\cancel{h^2}} \right)$$

$$\frac{E}{\Delta E} = 12\pi^2 = 118.435\,252\,8$$

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**\*11.33.** Prove that any two wave functions for a particle in a one-dimensional box of length  $a$  are orthogonal to each other; that is, they obey the relationship

$$\int_0^a \psi_m \psi_n dx = 0, \quad m \neq n$$

**Solution:**

Given: one-dimensional box of length  $a$ , two wave functions

Required: proof

To solve this problem, we take the wave functions for levels  $m$  and  $n$  in the form of Eq. 11. 148,

$$\psi_m = \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \text{ and } \psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

Substituting  $y = \frac{\pi x}{a}$  simplifies the problem. Therefore

$$\frac{dy}{dx} = \frac{\pi}{a}$$

$$dx = \frac{a}{\pi} dy$$

And the boundaries become,

$$x = 0; \quad y = \frac{\pi(0)}{a} = 0$$

$$x = a; \quad y = \frac{\pi(a)}{a} = \pi$$

Solving the integral, we get

$$\int_0^\pi \psi_m \psi_n dy$$

$$\int_0^\pi \sqrt{\frac{2}{\pi}} \sin my \sqrt{\frac{2}{\pi}} \sin ny dy$$

$$\frac{2}{\pi} \int_0^\pi \sin my \sin ny dy$$

The integral  $\int \sin my \sin ny dy$  is a standard integral with the solution

$$\int \sin my \sin ny dy = \frac{1}{2} \left[ \frac{\sin(m-n)y}{m-n} - \frac{\sin(m+n)y}{m+n} \right]$$

Therefore we get,

$$\int_0^\pi \sin my \sin ny dy = \frac{2}{\pi} \frac{1}{2} \left[ \frac{\sin(m-n)y}{m-n} - \frac{\sin(m+n)y}{m+n} \right]_0^\pi$$

$$\int_0^\pi \sin my \sin ny dy = \frac{1}{\pi} \left[ \frac{\sin(m-n)\pi}{m-n} - \frac{\sin(m+n)\pi}{m+n} - \frac{\sin(m-n)0}{m-n} + \frac{\sin(m+n)0}{m+n} \right]$$

$$\int_0^\pi \sin my \sin ny dy = \frac{1}{\pi} [0]$$

$$\int_0^\pi \sin my \sin ny dy = 0$$

As we can see, at the lower limit, both terms are zero since  $\sin 0 = 0$ . At the upper limit, both terms are also zero since  $m$  and  $n$  are integers, and any sine of any integer of  $\pi$  will return 0.

Therefore the integral is zero and the wave functions  $\psi_m$  and  $\psi_n$  are orthogonal.

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**11.34.** Use the trial function  $\Psi = x(a - x)$  and Eq. 11.247 to calculate an energy for a particle in a one-dimensional box of length  $a$ .

**Solution:**

Given:  $\Psi$ , Eq. 11.247, one-dimensional box of length  $a$

Required:  $E$

Energy is given by Eq. 11.247 as,

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$

The  $\hat{H}$  operator is given in Table 11.1 as,

$$-\frac{\hbar^2}{2m} \nabla^2 + \hat{E}_p$$

The potential energy,  $E_p$ , can be set to zero inside the box, and the Del-squared or Laplacian operator, is given by Eq. 11.81

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

For a one-dimensional box,

$$\nabla^2 = \frac{d^2}{dx^2}$$

Using  $\hbar = \frac{h}{2\pi}$ , and the boundaries of the box as 0 and  $a$ , we rewrite Eq. 11.247 as

$$E = \frac{\int_0^a \Psi \left( -\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} \right) dx}{\int_0^a \Psi^2 dx}$$
$$E = \frac{-\frac{\hbar^2}{8\pi^2 m} \int_0^a x(a-x) \left( \frac{d^2(x(a-x))}{dx^2} \right) dx}{\int_0^a x^2(a-x)^2 dx}$$

Solving the denominator and numerator separately provides a much easier way to obtain the result.

The numerator is,

$$\begin{aligned}
& -\frac{h^2}{8\pi^2 m} \int_0^a x(a-x) \left( \frac{d^2(x(a-x))}{dx^2} \right) dx \\
&= -\frac{h^2}{8\pi^2 m} \int_0^a x(a-x) \left( \frac{d^2(ax-x^2)}{dx^2} \right) dx \\
&= -\frac{h^2}{8\pi^2 m} \int_0^a x(a-x) \left( \frac{d(a-2x)}{dx} \right) dx \\
&= -\frac{h^2}{8\pi^2 m} \int_0^a x(a-x)(-2) dx \\
&= \frac{h^2}{4\pi^2 m} \int_0^a (ax-x^2) dx \\
&= \frac{h^2}{4\pi^2 m} \left[ \frac{ax^2}{2} - \frac{x^3}{3} \right]_0^a \\
&= \frac{h^2}{4\pi^2 m} \left[ \frac{a(a)^2}{2} - \frac{(a)^3}{3} - 0 \right] \\
&= \frac{h^2}{4\pi^2 m} \left[ \frac{a^3}{2} - \frac{a^3}{3} \right] \\
&= \frac{a^3 h^2}{24\pi^2 m}
\end{aligned}$$

The denominator is,



$$\begin{aligned} & \int_0^a x^2 (a-x)^2 dx \\ &= \int_0^a x^2 (a^2 - 2ax + x^2) dx \\ &= \int_0^a (a^2 x^2 - 2ax^3 + x^4) dx \\ &= \left[ a^2 \frac{x^3}{3} - a \frac{x^4}{2} + \frac{x^5}{5} \right]_0^a \\ &= \left[ a^2 \left( \frac{a^3}{3} \right) - a \left( \frac{a^4}{2} \right) + \left( \frac{a^5}{5} \right) - 0 \right] \\ &= \frac{a^5}{3} - \frac{a^5}{2} + \frac{a^5}{5} \\ &= a^5 \left( \frac{1}{3} - \frac{1}{2} + \frac{1}{5} \right) \\ &= \frac{a^5}{30} \end{aligned}$$

Therefore  $E$  is,

$$E = \frac{a^3 h^2}{24\pi^2 m} \div \frac{a^5}{30}$$

$$E = \frac{a^3 h^2}{24\pi^2 m} \times \frac{30}{a^5}$$

$$E = \frac{30h^2}{3 \times 8\pi^2 m a^3}$$

$$E = \frac{10}{\pi^2} \left( \frac{h^2}{8ma^3} \right)$$

$$\boxed{E = \frac{5h^2}{4\pi^2 ma^2}}$$

Notice that for  $n = 1$ , the exact energy is

$$\frac{h^2}{8ma^3}$$

And that in this case we have

$\frac{10}{\pi^2}$  times the exact energy.

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- 11.35. a.** At a node, a wave function passes through zero. For the problem of the particle in a box, how many nodes are there for  $n = 2$  and  $n = 3$ ?
- b.** From the expression for the radial function for the 3s electron (Table 11.4), obtain expressions for the position of the radial nodes (i.e., the nodes in the solution of the radial equation) in terms of  $Z$  and  $a_0$ .

**Solution:**

Given: particle in a box,  $n = 2$  and  $n = 3$ , 3s electron, Table 11.4

Required: number of nodes, position of nodes in terms of  $Z$  and  $a_0$  ( $r$ )

- a. For  $n = 2$ , there is one node. For  $n = 3$ , there are two nodes. We do not count the points  $x = 0$  and  $x = a$ , where the wave function becomes zero but does not pass *through* it.
- b. From Table 11.4, we have the radial function for the 3s electron is,

$$R_{30} = \frac{1}{9\sqrt{3}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 6 - \frac{4Zr}{a_0} + \frac{4Z^2 r^2}{9a_0^2} \right) e^{-Zr/3a_0}$$

Since we know the nodes are at a position where the wave function passes through zero, we set the expression equal to zero to solve for  $r$ .

$$R_{30} = \frac{1}{9\sqrt{3}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 6 - \frac{4Zr}{a_0} + \frac{4Z^2 r^2}{9a_0^2} \right) e^{-Zr/3a_0} = 0$$

$$\cancel{\frac{1}{9\sqrt{3}}} \cancel{\left( \frac{Z}{a_0} \right)^{3/2}} \left( 6 - \frac{4Zr}{a_0} + \frac{4Z^2 r^2}{9a_0^2} \right) \cancel{e^{-Zr/3a_0}} = 0$$

$$6 - \frac{4Zr}{a_0} + \frac{4Z^2 r^2}{9a_0^2} = 0$$

$$6a_0^2 - 4Za_0 r + \frac{4Z^2}{9} r^2 = 0$$

We can solve for  $r$  using the quadratic equation.

$$r_{\pm} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$r_{\pm} = \frac{1}{2\left(\frac{4Z^2}{9}\right)} \left( 4Za_0 \pm \sqrt{(4Za_0)^2 - 4\left(\frac{4Z^2}{9}\right)(6a_0^2)} \right)$$

$$r_{\pm} = \frac{1}{\left(\frac{8Z^2}{9}\right)} \left( 4Za_0 \pm \sqrt{16Z^2a_0^2 - \frac{32Z^2a_0^2}{3}} \right)$$

$$r_{\pm} = \frac{9}{8Z^2} \left( 4Za_0 \pm \sqrt{16 - \frac{32}{3}} Za_0 \right)$$

$$r_{\pm} = \frac{9}{8Z^2} \left( 4Za_0 \pm \sqrt{\frac{16}{3}} Za_0 \right)$$

$$r_{\pm} = \frac{9}{8Z^2} \left( 4Za_0 \pm \frac{4}{\sqrt{3}} Za_0 \right)$$

$$r_{\pm} = \frac{9}{2} \frac{a_0}{Z} \left( 1 \pm \frac{1}{\sqrt{3}} \right)$$

$$\boxed{r_{\pm} = \frac{3}{2} \frac{a_0}{Z} (3 \pm \sqrt{3})}$$

Therefore the two radial nodes are located at distances of  $r = \frac{3}{2} \frac{a_0}{Z} (3 + \sqrt{3})$  and  $r = \frac{3}{2} \frac{a_0}{Z} (3 - \sqrt{3})$  from the nucleus.

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**11.36.** The vibration frequency of the  $N_2$  molecule corresponds to a wave number of  $2360\text{ cm}^{-1}$ . Calculate the zero-point energy and the energy corresponding to  $\nu = 1$ .

**Solution:**

Given:  $N_2$ ,  $\bar{\nu} = 2360\text{ cm}^{-1}$ ,  $\nu = 1$

Required: Zero-point energy

The zero-point energy at  $\nu = 1$  can be calculated using,

$$E = \frac{3}{2} h\nu_0$$

Frequency,  $\nu_0$ , is calculated from, Eq. 11.1,

$$c = \lambda\nu$$

$$\bar{\nu} = \frac{1}{\lambda}$$

$$\nu = \frac{c}{\lambda} = c\bar{\nu}$$

$$E = \frac{3}{2} hc\bar{\nu}$$

$$E = \frac{3}{2} (6.626 \times 10^{-34}\text{ J s}) (2.998 \times 10^{10}\text{ cm s}^{-1}) (2360\text{ cm}^{-1})$$

$$E = 7.03212079 \times 10^{-20}\text{ J}$$

$$\boxed{E = 7.032 \times 10^{-20}\text{ J}}$$

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\*11.37. If a rigid body rotates in the  $XY$  plane, about the  $Z$  axis, the angular momentum operator is

$$\hat{L} = -i\hbar \frac{\partial}{\partial \phi}$$

(see Figure 11.15). If the moment of inertia is  $I$ , what is the energy operator?

(For additional problems dealing with molecular vibrations and rotations, see Chapter 13.)

**Solution:**

Given: the angular momentum operator,  $I$

Required: energy operator

The energy is related to the angular momentum by Eq. 11.215,

$$E = E_k = \frac{L^2}{2I}$$

The energy, or Hamiltonian operator is therefore,

$$E = \frac{1}{2I} \left( -i\hbar \frac{\partial}{\partial \phi} \right)^2$$

$$E = \frac{1}{2I} \left( (-1)^2 i^2 \hbar^2 \frac{\partial^2}{\partial \phi^2} \right)$$

$$E = \frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$$

$$\hbar = \frac{h}{2\pi}$$

$$\boxed{E = \frac{-h^2}{8\pi^2 I} \frac{\partial^2}{\partial \phi^2}}$$

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**11.38.** Calculate the ionization energy of the hydrogen atom on the basis of the Bohr theory.

**Solution:**

Given: hydrogen atom

Required: ionization energy

The energy required to remove the electron from the lowest energy level in hydrogen ( $n_1 = 1$ ) to infinity, ( $n_2 = \infty$ ) is the ionization energy.

We use Eq. 11.50, Eq. 11.1 and the expression for energy,  $E = h\nu$ , to solve.

$$\bar{\nu} = \frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$c = \lambda \nu$$

$$\nu = \frac{c}{\lambda} = c\bar{\nu}$$

$$E = hcR \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$E = (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1}) (1.0968 \times 10^7 \text{ m}^{-1}) \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right)$$

$$E = 2.178\,765\,56 \times 10^{-18} \text{ J}$$

$$\boxed{E = 2.179 \times 10^{-18} \text{ J}}$$

In eV,

$$E = \frac{2.178\,765\,56 \times 10^{-18} \text{ J}}{1.602 \times 10^{-19} \text{ J eV}^{-1}}$$

$$E = 13.600\,284\,4 \text{ eV}$$

$$\boxed{E = 13.60 \text{ eV}}$$

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**11.39.** Calculate, on the basis of the Bohr theory, the linear velocity of an electron (mass =  $9.11 \times 10^{-31}$  kg) in the ground state of the hydrogen atom. To what de Broglie wavelength does this velocity correspond? Deduce an equation for the de Broglie wavelength, in a Bohr orbit of quantum number  $n$ , with  $Z = 1$ , in terms of  $a_0$  and  $n$ . What is the ratio of the circumference of a Bohr orbit of quantum number  $n$  to the de Broglie wavelength?

**Solution:**

Given:  $m = 9.11 \times 10^{-31}$  kg,  $n$ ,  $Z = 1$

Required:  $u$ ,  $\lambda_{\text{de Broglie}}$ ,  $\lambda_{\text{de Broglie}}$  (expression),  $C : \lambda_{\text{de Broglie}}$  (expression)

Velocity is given in Eq. 11.39 as,

$$L = mur = n \frac{h}{2\pi} = n\hbar \quad (n=0,1,2,\dots)$$

Since we are told the electron is in the ground state of the hydrogen atom,  $n = 1$  and velocity is therefore,

$$u = \frac{h}{2\pi mr}$$

From Eq. 11.44, we take  $r = a_0$ . This is because  $a_0$  is a length and is the radius of the orbit for  $n = 1$  for the hydrogen atom itself ( $Z = 1$ ).

The length  $a_0$  is known as the Bohr radius and has a value of 52.92 pm (1 picometre =  $10^{-12}$  m).

$$u = \frac{(6.626 \times 10^{-34} \text{ J s})}{2\pi (9.11 \times 10^{-31} \text{ kg})(52.92 \times 10^{-12} \text{ m})}$$

$$u = 2187425.903 \text{ m s}^{-1}$$

$$\boxed{u = 2.19 \times 10^6 \text{ m s}^{-1}}$$

The de Broglie wavelength is given by Eq. 11.56,

$$\lambda = \frac{h}{p} = \frac{h}{mu}$$



Solving, using the velocity determined above we get,

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.11 \times 10^{-31} \text{ kg})(2187425.903 \text{ m s}^{-1})}$$

$$\lambda = 3.32506166 \times 10^{-10} \text{ m}$$

$$\boxed{\lambda = 3.33 \times 10^{-10} \text{ m} = 333 \text{ pm}}$$

To find the de Broglie expression for wavelength in terms of  $a_0$  and  $n$  we use Eq. 11.56 and Eq. 11.39.

$$u = \frac{nh}{2\pi mr}$$

$$\frac{2\pi r}{n} = \frac{h}{mu}$$

$$\lambda = \frac{h}{mu} = \frac{2\pi r}{n}$$

From Eq. 11.43 with  $Z = 1$ ,

$$r = \frac{n^2}{Z} a_0$$

$$r = a_0 n^2$$

$$\lambda = \frac{2\pi}{n} (a_0 n^2)$$

$$\boxed{\lambda = 2\pi a_0 n}$$

The expression for circumference is  $C = 2\pi r$ , hence

$C = 2\pi n^2 a_0$  and the ratio  $C : \lambda$  is

$$C : \lambda = \frac{\cancel{2\pi a_0} n^2}{\cancel{2\pi a_0} n}$$

$$\boxed{C : \lambda = n}$$

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**11.40.** For a hydrogen-like atom (a one-electron system with a charge number of  $Z$ ), find the radius of the sphere on which the probability of finding the 1s electron is a maximum. Compare the result to the expression of Eq. 11.44.

**Solution:**

Given: a one-electron system, charge of  $Z$

Required:  $r$

The radius of the sphere of maximum probability corresponds to the maximum in the radial probability function, given in Section 11.8 by

$$4\pi r^2 \psi_{1s}^2$$

We find the maximum  $r$  by differentiating the radial probability function with respect to  $r$  and setting it equal to zero.

Using Eq. 11.193, and  $Z$ , we solve to obtain  $r$ .

$$\psi_{1s}^2 = \frac{e^{-2r/a_0}}{\pi a_0^3}$$

$$P = 4\pi r^2 \left( \frac{1}{\pi} \right) \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0}$$

$$\frac{dP}{dr} = \frac{d}{dr} \left( 4\pi r^2 \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0} \right) = 0$$

$$8\pi r \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0} + 4\pi r^2 \left( \frac{Z}{a_0} \right)^3 \left( \frac{-2Z}{a_0} \right) e^{-2Zr/a_0} = 0$$

$$\cancel{8\pi \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0}} \left( r \left( 1 - r \frac{Z}{a_0} \right) \right) = 0$$

$$r \left( 1 - r \frac{Z}{a_0} \right) = 0$$

$$r = 0, 1 - r \frac{Z}{a_0} = 0$$

$$\boxed{r = \frac{a_0}{Z}}$$

We ignore the  $r = 0$  value since it does not make sense for the radius to be zero. The expression for  $r$  obtained here is identical to Eq. 11.43 for the case of a 1s electron.

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**\*11.41.** Calculate the reduced masses of the hydrogen and deuterium atoms, using the following masses for the particles:

Electron:  $9.1095 \times 10^{-31} \text{ kg}$

Proton:  $1.6727 \times 10^{-27} \text{ kg}$

Deuterium nucleus:  $3.3434 \times 10^{-27} \text{ kg}$

**a.** Explain qualitatively what effect the different reduced masses will have on the Bohr radii and therefore on the positions of the lines in the atomic spectra.

**b.** The Balmer spectrum of hydrogen has a line of wavelength 656.47 nm. Deduce the wavelength of the corresponding line in the spectrum of deuterium.

**Solution:**

Given: particle masses above,  $\lambda = 656.47 \text{ nm}$

Required:  $\mu$ , a, b,

The reduced mass is calculated from Eq. 11.152,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

For hydrogen we get,

$$\mu_{\text{H}} = \frac{(m_e m_{\text{H}})}{m_e + m_{\text{H}}}$$

$$\mu_{\text{H}} = \frac{(9.1095 \times 10^{-31} \text{ kg})(1.6727 \times 10^{-27} \text{ kg})}{9.1095 \times 10^{-31} \text{ kg} + 1.6727 \times 10^{-27} \text{ kg}}$$

$$\mu_{\text{H}} = 9.10454 \times 10^{-31} \text{ kg}$$

$$\boxed{\mu_{\text{H}} = 9.1045 \times 10^{-31} \text{ kg}}$$

$$\mu_{\text{D}} = \frac{(m_e m_{\text{D}})}{m_e + m_{\text{D}}}$$

$$\mu_{\text{D}} = \frac{(9.1095 \times 10^{-31} \text{ kg})(3.3434 \times 10^{-27} \text{ kg})}{9.1095 \times 10^{-31} \text{ kg} + 3.3434 \times 10^{-27} \text{ kg}}$$

$$\mu_{\text{D}} = 9.10702 \times 10^{-31} \text{ kg}$$

$$\boxed{\mu_{\text{D}} = 9.1070 \times 10^{-31} \text{ kg}}$$

a. The reduced mass and the Bohr radius are related by Eq. 11.44,

$$a_0 = \frac{h^2 \epsilon_0}{\pi \mu e^2}$$

The Bohr radius is inversely proportional to the reduced mass, therefore it is slightly smaller for deuterium than it is for hydrogen.

Additionally, the Bohr radius is inversely proportional to the energies. Therefore, the energies are slightly greater for deuterium than it is for hydrogen. The frequencies of the transitions are therefore slightly greater for deuterium, and the wavelengths are slightly shorter.

b. The wavelengths are in the inverse ratio of the reduced masses, and therefore we have the ratio,

$$\frac{\lambda_{\text{H}}}{\lambda_{\text{D}}} = \frac{9.1045}{9.1070}$$

The wavelength of the line in the spectrum of deuterium is therefore,

$$\lambda = \frac{9.1045}{9.1070} \times 656.47 \text{ nm}$$

$$\lambda = 656.289\,789\,7 \text{ nm}$$

$$\boxed{\lambda = 656.29 \text{ nm}}$$

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**11.42.** Calculate the wavelength and energy corresponding to the  $n = 4$  to  $n = 5$  transition in the hydrogen atom.

**Solution:**

Given:  $n = 4, n = 5$ , hydrogen atom

Required:  $\lambda, E$

From Eq. 11.50, we can calculate the wavelength,

$$\tilde{\nu} = \frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\lambda = \left( R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \right)^{-1}$$

$$\lambda = \left( 1.0968 \times 10^7 \text{ m}^{-1} \left( \frac{1}{4^2} - \frac{1}{5^2} \right) \right)^{-1}$$

$$\lambda = 4.05219 \times 10^{-6} \text{ m}$$

$$\boxed{\lambda = 4.0522 \times 10^{-6} \text{ m}}$$

Energy is determined from Eq. 11.1 and  $E = h\nu$ ,

$$E = h\nu$$

$$c = \lambda\nu$$

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1})}{4.05219 \times 10^{-6} \text{ m}}$$

$$E = 4.90222 \times 10^{-20} \text{ J}$$

$$\boxed{E = 4.902 \times 10^{-20} \text{ J}}$$

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**11.43.** Calculate, in joules and in atomic units, the potential energy of an electron in the  $n = 2$  orbit of the hydrogen atom.

**Solution:**

Given:  $n = 2$ , hydrogen atom

Required:  $E_p$

We use Eq. 11.48, with  $Z = 1$  for a hydrogen atom to solve for  $E_p$ ,

$$E_p = -\frac{Z^2 e^2}{4\pi \epsilon_0 n^2 a_0}$$
$$E_p = -\frac{(1.602 \times 10^{-19} \text{ C})^2}{4\pi (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) 2^2 (52.92 \times 10^{-12} \text{ m})}$$

$$E_p = -1.08967 \times 10^{-18} \text{ J}$$

$$\boxed{E_p = -1.090 \times 10^{-18} \text{ J}}$$

In atomic units of  $\frac{e^2}{4\pi \epsilon_0 a_0}$ ,

$$E_p = -\frac{1^2}{2^2}$$

$$\boxed{E_p = -0.25 \text{ au}}$$

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**11.44.** The first ionization energy of the Li atom is 5.39 eV. Estimate an effective nuclear charge  $Z_{\text{eff}}$  for the valence electron in the Li atom.

**Solution:**

Given:  $E_{\text{ionization}} = 5.39 \text{ eV}$

Required:  $Z_{\text{eff}}$

Problems 11.44 and 11.45 are conveniently worked out with reference to Problem 11.38, where we determined the ionization energy for hydrogen as 13.60 eV. From Eq. 11.49,

$$E = E_k + E_p = -\frac{Z^2 e^2}{8\pi \epsilon_0 n^2 a_0}$$

the first ionization energy is proportional to  $\frac{Z_{\text{eff}}^2}{n^2}$ .

For H,  $Z_{\text{eff}} = 1$  and  $n = 1$ , hence,

$$I = 13.60 \text{ eV} \left( \frac{Z_{\text{eff}}^2}{n^2} \right)$$

$$I = 13.60 \text{ eV} \left( \frac{1^2}{1^2} \right)$$

$$I = 13.60 \text{ eV}$$

For Li,  $n = 2$ , hence,

$$I = 13.60 \text{ eV} \left( \frac{Z_{\text{eff}}^2}{n^2} \right)$$

$$Z_{\text{eff}} = \sqrt{\frac{n^2 I}{13.60 \text{ eV}}}$$

$$Z_{\text{eff}} = \sqrt{\frac{2^2 (5.39 \text{ eV})}{13.60 \text{ eV}}}$$

$$Z_{\text{eff}} = 1.259\,084\,635$$

$$\boxed{Z_{\text{eff}} = 1.26}$$

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**11.45.** The first ionization energy of the Na atom is 5.14 eV. Estimate the effective nuclear charge  $Z_{\text{eff}}$  for the valence electron in the Na atom.

**Solution:**

Given:  $E_{\text{ionization}} = 5.14 \text{ eV}$

Required:  $Z_{\text{eff}}$

For Na,  $n = 3$ , hence,

$$I = 13.60 \text{ eV} \left( \frac{Z_{\text{eff}}^2}{n^2} \right)$$

$$Z_{\text{eff}} = \sqrt{\frac{3^2 I}{13.60 \text{ eV}}}$$

$$Z_{\text{eff}} = \sqrt{\frac{3^2 (5.14 \text{ eV})}{13.60 \text{ eV}}}$$

$$Z_{\text{eff}} = 1.844\ 307\ 618$$

$$\boxed{Z_{\text{eff}} = 1.84}$$

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**\*11.46.** Use Slater's method (Section 11.13) to determine the effective nuclear charge for

- a. a 3s electron in the chlorine atom,
- b. a 3p electron in the phosphorus atom, and
- c. the 4s electron in the potassium atom.

**Solution:**

Given: a – c,

Required:  $Z_{\text{eff}}$

Using the Slater method, we find  $Z_{\text{eff}}$  from Eq. 254,

$$Z_{\text{eff}} = Z - \sigma$$

We use the four rules to help solve for  $Z_{\text{eff}}$ .

- a. The nuclear charge of Cl is,  $Z = 17$ . We then subtract:
- 0.30 for the other 3s electron
  - $5 \times 0.35$  for the five 3p electrons
  - $8 \times 0.85$  for the eight 2s and 2p electrons,
  - $2 \times 1.00$  for the two 1s electrons

$$Z_{\text{eff}} = 17 - 0.30 - 5 \times 0.35 - 8 \times 0.85 - 2 \times 1.00$$

$$\boxed{Z_{\text{eff}} = 6.15}$$

- b. The nuclear charge of P is,  $Z = 15$ . We then subtract:
- $2 \times 0.30$  for the 3s electron
  - $2 \times 0.35$  for the other 3p electrons
  - $8 \times 0.85$  for the eight 2s and 2p electrons,
  - $2 \times 1.00$  for the two 1s electrons

$$Z_{\text{eff}} = 15 - 2 \times 0.30 - 2 \times 0.35 - 8 \times 0.85 - 2 \times 1.00$$

$$\boxed{Z_{\text{eff}} = 4.9}$$

- c. The nuclear charge of K is,  $Z = 19$ . We then subtract:
- $8 \times 0.85$  for the eight 2s and 2p electrons,

$$10 \times 1.00 \text{ for the } 1s, 2s \text{ and } 2p \text{ electrons}$$
$$Z_{\text{eff}} = 19 - 8 \times 0.85 - 10 \times 1.00$$

$$Z_{\text{eff}} = 2.2$$

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**\*11.47.** A normalized Slater orbital for the 1s orbital in the helium atom is

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z_{\text{eff}}}{a_0} \right)^{3/2} \exp(-Z_{\text{eff}} r/a_0)$$

where  $Z_{\text{eff}}$  is the effective charge number. It leads to the following expression for the energy

$$E = \frac{e^2}{a_0} \left( Z_{\text{eff}}^2 - \frac{27}{8} Z_{\text{eff}} \right).$$

Treat  $Z_{\text{eff}}$  as a variation parameter, and calculate a minimum energy in terms of  $e$  and  $a_0$ . Why is the optimum value of  $Z_{\text{eff}}$  different from the actual charge number?

**Solution:**

Given:  $E$

Required:  $E_{\text{min}}$  in terms of  $e$  and  $a_0$ , optimum  $Z_{\text{eff}}$

To solve we minimize  $E$  with respect to  $Z_{\text{eff}}$ ,

$$\frac{dE}{dZ_{\text{eff}}} = \frac{e^2}{a_0} \left( 2Z_{\text{eff}} - \frac{27}{8} \right) = 0$$

$$\frac{e^2}{a_0} \left( 2Z_{\text{eff}} - \frac{27}{8} \right) = 0$$

$$2Z_{\text{eff}} - \frac{27}{8} = 0$$

$$\boxed{Z_{\text{eff}} = \frac{27}{16}}$$

Solving for  $E_{\text{min}}$  in terms of  $e$  and  $a_0$ , we get,

$$Z_{\text{eff}} = \frac{27}{16}$$

$$E_{\text{min}} = \frac{e^2}{a_0} \left( \left( \frac{27}{16} \right)^2 - \frac{27}{8} \left( \frac{27}{16} \right) \right)$$

$$E_{\text{min}} = - \left( \frac{729}{256} \right) \frac{e^2}{a_0}$$

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**\*11.48.** Use the wave function for the 1s orbital of the hydrogen atom, given in Table 11.5, to obtain an expression for the probability that the electron lies between the distance  $r$  and  $r + dr$  from the nucleus. (Use spherical polar coordinates, for which the volume element is  $r^2 dr \sin \theta d\theta d\phi$ .)

**Solution:**

Given: Table 11.5

Required:  $P$  in spherical polar coordinates

The expression for the wave function for the 1s orbital of the hydrogen atom is given in Table 11.5 as,

$$\psi_{1s} = \psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

To find  $P$ , we must solve for,

$$\int_r^{r+dr} \psi^* \psi = \frac{1}{\pi a_0^3} e^{-2r/a_0} dr$$

Multiplying by the volume element, integrating  $\theta$  from 0 to  $\pi$  and  $\phi$  from 0 to  $2\pi$ , we convert to spherical polar coordinates.

$$\int_0^\pi \int_0^{2\pi} \psi^* \psi = \frac{1}{\pi a_0^3} e^{-2r/a_0} r^2 dr \sin \theta d\theta d\phi$$

separating the integrals,

$$\int_0^\pi \sin \theta d\theta = -\cos \theta \Big|_0^\pi$$

$$\int_0^\pi \sin \theta d\theta = -(-1 - 1)$$

$$\int_0^\pi \sin \theta d\theta = 2$$

$$\int_0^{2\pi} d\phi = \phi \Big|_0^{2\pi}$$

$$\int_0^{2\pi} d\phi = 2\pi$$

Therefore we get,

$$P = 4\pi \frac{1}{a_0^3} e^{-2r/a_0} r^2 dr$$

$$P = \frac{4}{a_0^3} r^2 e^{-2r/a_0} dr$$

[Back to Problem 11.48](#)

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**\*11.49.** Unsöld's theorem (Section 11.8) states that, for a given value of  $l$ , the sum of the values of

$$\sum_{l,m} [\Theta_{l,m}(\theta)\Phi_m(\phi)]^2$$

is independent of  $\theta$  and  $\phi$ , i.e., is a constant. Write all these functions for the 2p orbitals (see Tables 11.2 and 11.3), and show that their sum shows no angular dependence.

**Solution:**

Given: Unsöld's theorem, Tables 11.2 and 11.3

Required: functions for the 2p orbitals, show there is no angular dependence in their sum

From Tables 11.2 and 11.3, we have the following for  $l = 1$  and  $m_l = -1, 0, 1$ .

$$\Phi_1 = \frac{\cos \phi}{\sqrt{\pi}} \quad \Theta_{10} = \frac{\sqrt{6}}{2} \cos \theta$$

$$\Phi_0 = \frac{1}{\sqrt{2\pi}} \quad \Theta_{1\pm 1} = \frac{\sqrt{3}}{2} \sin \theta$$

$$\Phi_{-1} = \frac{\sin \phi}{\sqrt{\pi}}$$

The functions for the 2p orbitals are therefore,

$$\Theta_{10}\Phi_0 = \frac{\sqrt{6}}{2} \cos \theta \frac{1}{\sqrt{2\pi}}$$

$$\Theta_{11}\Phi_1 = \frac{\sqrt{3}}{2} \sin \theta \frac{1}{\sqrt{\pi}} \cos \phi$$

$$\Theta_{1-1}\Phi_{-1} = \frac{\sqrt{3}}{2} \sin \theta \frac{1}{\sqrt{\pi}} \sin \phi$$

The sum of their squares is,

$$\begin{aligned} &= \left( \frac{\sqrt{6}}{2} \cos \theta \frac{1}{\sqrt{2\pi}} \right)^2 + \left( \frac{\sqrt{3}}{2} \sin \theta \frac{1}{\sqrt{\pi}} \cos \phi \right)^2 + \left( \frac{\sqrt{3}}{2} \sin \theta \frac{1}{\sqrt{\pi}} \sin \phi \right)^2 \\ &= \frac{6}{4} \cos^2 \theta \frac{1}{2\pi} + \frac{3}{4} \sin^2 \theta \frac{1}{\pi} \cos^2 \phi + \frac{3}{4} \sin^2 \theta \frac{1}{\pi} \sin^2 \phi \\ &= \frac{3}{4\pi} (\cos^2 \theta + \sin^2 \theta (\cos^2 \phi + \sin^2 \phi)) \\ &\quad \cos^2 \phi + \sin^2 \phi = 1 \\ &= \frac{3}{4\pi} (\cos^2 \theta + \sin^2 \theta) \\ &= \frac{3}{4\pi} \end{aligned}$$

This solution is independent of  $\theta$  and  $\phi$ .

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CHAPTER

# 13

Foundations of  
Chemical Spectroscopy

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# Problems and Solutions

## Chapter 13

### Absorption of Radiation

- 13.1.** The molar absorption coefficient of human hemoglobin (molecular weight 64 000) is  $532 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$  at 430 nm. A solution of hemoglobin in a cuvette having a light path of 1 cm was found at that wavelength to have a transmittance of 76.7%. Calculate the concentration in  $\text{mol dm}^{-3}$  and in  $\text{g dm}^{-3}$ .

[Solution](#)

- 13.2.** A spectrophotometer has a meter that gives a reading directly proportional to the amount of light reaching the detector. When the light source is off, the reading is zero. With pure solvent in the light path, the meter reading is 78; with a 0.1 *M* solution of a solute in the same solvent, the meter reading is 55. The light path is 0.5 cm. Calculate the absorbance, the transmittance, and the molar absorption coefficient.

[Solution](#)

- 13.3.** The transmission of a potassium chromate solution was measured at a wavelength of 365 nm using a cell with a 1.0-cm path length. The data are as follows:

Transmission	0.357	0.303	0.194	0.124
Conc. $\times 10^4/\text{mol dm}^{-3}$	0.90	1.10	1.50	1.90

Calculate the molar Napierian absorbance and the molar decadic absorbance.

[Solution](#)

- 13.4.** An aqueous solution containing 0.95 g of oxygenated myoglobin ( $M_r = 18\,800$ ) in  $100 \text{ cm}^3$  gave a transmittance of 0.87 at 580 nm, with a path length of 10.0 cm. Calculate the molar absorption coefficient.

[Solution](#)

- 13.5.** A substance in aqueous solution at a concentration of 0.01 *M* shows an optical transmittance of 28% with a path length of 2 mm. Calculate the molar absorption coefficient of the solute. What would be the transmittance in a cell 1-cm thick?

[Solution](#)

- 13.6.** The molar absorption coefficient of hemoglobin at 430 nm is  $532 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . A solution of hemoglobin was found to have an absorbance of 0.155 at 430 nm, with a light path of 1.00 cm. Calculate the concentration.

[Solution](#)

- 13.7.** A  $10\ \mu\text{M}$  solution of a substance gave an absorbance of 0.1028 with a light path of 1 cm. Calculate the molar absorption coefficient. What would be the percentage light transmittance of a  $1\text{-}\mu\text{m}$  solution with the same light path?
- [Solution](#)
- 13.8.** Two substances of biological importance,  $\text{NAD}^+$  and  $\text{NADH}$ , have equal absorption coefficients,  $1.8 \times 10^4\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ , at 260 nm (a wavelength at which absorption coefficients are equal is known as the *isosbestic point*<sup>6</sup>). At 340 nm,  $\text{NAD}^+$  does not absorb at all, but  $\text{NADH}$  has an absorption coefficient of  $6.22 \times 10^3\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ . A solution containing both substances had an absorbance of 0.215 at 340 nm and of 0.850 at 260 nm. Calculate the concentration of each substance.
- [Solution](#)
- 13.9.** The transmittance of a  $0.01\ \text{M}$  solution of bromine in carbon tetrachloride, with a path length of 2 mm, is 28%. Calculate the molar absorption coefficient of bromine at that wavelength. What would the percentage transmittance be in a cell 1-cm thick?
- [Solution](#)
- 13.10.** An acid  $\text{HA}$  ionizes in aqueous solution into  $\text{H}^+$  and  $\text{A}^-$  ions. At a wavelength of 430 nm  $\text{HA}$  does not absorb light, but  $\text{A}^-$  does so with an absorption coefficient of  $458\ \text{dm}^3\ \text{cm}^{-1}\ \text{mol}^{-1}$ . A solution of the acid at a concentration of  $0.1\ \text{M}$  was found to have a transmittance of 1.47% at 430 nm with a path length of 1 cm and at  $25\ ^\circ\text{C}$ . Calculate the dissociation constant of  $\text{HA}$  at  $25\ ^\circ\text{C}$ , and  $\Delta G^\circ$  for the dissociation process.
- [Solution](#)

### Atomic Spectra

- 13.11.** In the Balmer series of the hydrogen atom, the first emission line is observed at 656.3 nm. Calculate the value of the Rydberg constant. What is the energy of the light quanta emitted during the transition?
- [Solution](#)
- 13.12.** The ground state of the Li atom has the electronic configuration  $1s^2 2s^1$ . What is its spectroscopic term? If the 2s electron is excited to the 2p state, what terms are then possible?
- [Solution](#)
- 13.13.** Suppose that an excited state of the carbon atom has the electronic configuration  $1s^2 2s^2 2p^1 3p^1$ . What are the possible spectroscopic terms?
- [Solution](#)

<sup>6</sup>From the Greek prefix *iso-*, the same, and *sbestos*, quench. This word is sometimes incorrectly written as “isobestic.”

**13.14.** What are the terms for the following electronic configurations?

- a. Na ( $1s^2 2s^2 2p^6 3p^1$ )
- b. Sc ( $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ )

[Solution](#)

**13.15.** What values of  $J$  may arise in the following terms?



[Solution](#)

**\*13.16.** Calculate the Landé-g-factor for a  $^2P_{1/2}$  level. What would be the anomalous Zeeman splitting for this level in a magnetic field of 4.0 T?

[Solution](#)

**\*13.17.** Calculate the spacing between the lines for a  $^3D_1 \rightarrow ^3P_0$  transition, in an anomalous Zeeman experiment with a magnetic field of 4.0 T.

[Solution](#)

### Rotational and Microwave Spectra

**13.18.** The separation between neighboring lines in the pure rotational spectrum of  $^{35}\text{Cl}^{19}\text{F}$  is found to be  $1.023\text{ cm}^{-1}$ . Calculate the interatomic distance.

[Solution](#)

**13.19.** The lines in the pure rotational spectrum of HF are  $41.9\text{ cm}^{-1}$  apart. Calculate the interatomic distance. Predict the separation between the lines for DF and TF.

[Solution](#)

**13.20.** In the microwave spectrum of  $^{12}\text{C}^{16}\text{O}$  the separation between lines has been measured to be 115270 MHz. Calculate the interatomic distance.

[Solution](#)

**\*13.21.** The  $J = 0 \rightarrow J = 1$  line in the microwave absorption spectrum of  $^{12}\text{C}^{16}\text{O}$  and of  $^{13}\text{C}^{16}\text{O}$  was measured by Gillam et al., [*Phys. Rev.* 78, 140(1950)]. In its ground vibrational state, the former has the value  $3.842\,35\text{ cm}^{-1}$  and the latter, the value  $3.673\,37\text{ cm}^{-1}$ . Calculate

- a. the bond length of the  $^{12}\text{C}^{16}\text{O}$  molecule,
- b. the relative atomic mass of  $^{13}\text{C}$ ,
- c. the bond length of the  $^{13}\text{C}^{16}\text{O}$  molecule.

[Solution](#)



- 13.22.** The microwave spectrum of  $^{16}\text{O}^{12}\text{C}^{32}\text{S}$  shows absorption lines separated by 12.163 GHz. That of  $^{16}\text{O}^{12}\text{C}^{34}\text{S}$  shows lines separated by 11.865 GHz. The determination of the bond distances involves solving two simultaneous quadratic equations, which is best done by successive approximations. To avoid all that labor, simply confirm that the results are consistent with  $r(\text{O—C}) = 116 \text{ pm}$  and  $r(\text{C—S}) = 156 \text{ pm}$ .

[Solution](#)

### Vibrational-Rotational and Raman Spectra

- 13.23.** The maximum potential energy that a diatomic molecule can store is  $\frac{1}{2}kx^2$ , where  $x$  is the amplitude of vibration. If the force constant  $k$  is  $1.86 \times 10^3 \text{ N m}^{-1}$ , calculate the maximum amplitude of vibration for the CO molecule in the  $\nu = 0$  vibrational state. Compare this to the bond length obtained in Problem 13.21. Use the value of  $u_r$  in that problem.

[Solution](#)

- 13.24.** Consider the following molecules:  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NH}_3$ , and  $\text{SF}_6$ . Which of them will give
- a pure rotational spectrum,
  - a vibrational-rotational spectrum,
  - a pure rotational Raman spectrum,
  - a vibrational Raman spectrum?

[Solution](#)

- 13.25.** Analysis of the vibrational-rotational spectrum of the  $\text{H}^{35}\text{Cl}$  molecule shows that its fundamental vibrational frequency  $\nu_0$  is  $2988.9 \text{ cm}^{-1}$ . Calculate the force constant of the  $\text{H—Cl}$  bond.

[Solution](#)

- 13.26.** A few transitions in the P and R branches of the infrared spectrum of  $\text{H}^{35}\text{Cl}$  spectrum are identified below.

$J''$	0	1	2	3	4	5	6
P ( $\text{cm}^{-1}$ )		2865.10	2843.62	2821.56	2798.94	2775.76	2752.04
R ( $\text{cm}^{-1}$ )	2906.24	2925.90	2944.90	2963.29	2981.00	2998.04	

Using Eqs. 13.134 or 13.135 as appropriate, calculate  $\tilde{\nu}_0$  and the rotational constant  $\tilde{B}$ .

[Solution](#)

**13.27.** Comparison of the results of Problem 13.26 to experimental values for  $\text{H}^{35}\text{Cl}$  ( $\tilde{\nu}_0 = 2990 \text{ cm}^{-1}$ , and  $\tilde{B} = 10.59 \text{ cm}^{-1}$ ) shows that Eqs. 13.134 and 13.135 do not accurately relate the observed transitions to the rotational quantum numbers. Much of the error results from not taking the anharmonicity of the potential energy curve into account. Using the definition (see Eq. 13.138)  $T_{v,J} = (v + \frac{1}{2})\tilde{\nu}_0 - (v + \frac{1}{2})^2 \tilde{\nu}_0 x_e + J(J+1)\tilde{B}$ , derive a more accurate expression for  $\Delta T_{v,J}$  for the  $v'' = 0 \rightarrow v' = 1$  transitions of a diatomic molecule. [Even this is an approximate treatment because we are ignoring the coupling of rotations with vibrations.]

[Solution](#)

**13.28.** From the results of Problems 13.26 and 13.27 and the experimental value of  $\tilde{\nu}_0$  for  $\text{H}^{35}\text{Cl}$  given in Problem 13.27, estimate the value of the anharmonicity constant  $x_e$ . Use the average of the P and R branch values for  $\tilde{\nu}_0$  from Problem 13.26.

[Solution](#)

**13.29.** The vibrational Raman spectrum of  $^{35}\text{Cl}_2$  shows series of Stokes and anti-Stokes lines; the separation between the lines in each of the two series is  $0.9752 \text{ cm}^{-1}$ . Estimate the bond length in  $\text{Cl}_2$ .

[Solution](#)

**13.30.** The dissociation energy of  $\text{H}_2$  is  $432.0 \text{ kJ mol}^{-1}$  and the fundamental vibrational frequency of the molecule is  $1.257 \times 10^{14} \text{ s}^{-1}$ . Calculate the classical dissociation energy. Estimate the zero-point energies of HD and  $\text{D}_2$  and their dissociation energies.

[Solution](#)

**13.31.** A molecule  $\text{AB}_2$  is known to be linear but it is not known whether it is  $\text{B—A—B}$  or  $\text{A—B—B}$ . Its infrared spectrum is found to show bands corresponding to three normal modes of vibration. Which is the structure?

[Solution](#)

**13.32.** The frequency of the O—H stretching vibration in  $\text{CH}_3\text{OH}$  is  $3300 \text{ cm}^{-1}$ . Estimate the frequency of the O—D stretching vibration in  $\text{CH}_3\text{OD}$ .

[Solution](#)

**13.33.** The spectroscopic constants for the OH radical are  $\tilde{\nu}_0 = 3737.76 \text{ cm}^{-1}$ ,  $\tilde{\nu}_0 x_e = 84.8813 \text{ cm}^{-1}$ ,  $\tilde{B} = 18.9108 \text{ cm}^{-1}$ . Predict the frequencies at which (a) the P branch transitions ending in, and (b) the R branch beginning in,  $J = 0, 1, 2$  will be observed.

[Solution](#)

**13.34.** Irradiation of acetylene with mercury radiation at  $435.83 \text{ nm}$  gives rise to a Raman line at  $476.85 \text{ nm}$ . Calculate the vibrational frequency that corresponds to this shift.

[Solution](#)

**13.35.** The fundamental vibrational frequency of  $\text{H}^{127}\text{I}$  is  $2309.5 \text{ cm}^{-1}$ . Calculate the force constant of the bond.

[Solution](#)

**\*13.36.** The following are some normal modes of vibration for several molecules:

[[Image]]

In each case, determine the point group and refer to Appendix E on p. 1028 to determine whether the vibration is active in the infrared and in the Raman spectrum. Then check your conclusions by reference to the appendix to this chapter (p. 707).

[Solution](#)

**\*13.37.** Prove that the force constant  $k$  corresponding to the Morse potential function (Eq. 13.146) at small bond extensions is

$$k = 2D_e a^2$$

Calculate the vibration frequency  $\nu_0$  on the basis of the following Morse parameters for  $\text{H}^{35}\text{Cl}$ :

$$D_e = 4.67 \text{ eV}$$

$$a = 1.85 \times 10^8 \text{ cm}^{-1}$$

[Solution](#)

**\*13.38.** The Morse function is only one of several models used to describe the behavior of the potential energy of diatomic molecules. A popular and very accurate model introduced by Murrell and Sorbie [*J. Chem. Soc., Faraday Trans. 2*, 70, 1552(1974)] is the so-called “Extended Rydberg function,” which is written as

$$E_p(x) = -D_e(1 + a_1x + a_2x^2 + a_3x^3)e^{-a_1x},$$

where  $x = r - r_e$ , as in the case of the Morse potential of Eq. 13.146, and the  $a_i$  are constants for a given molecule.

**a.** Derive an expression for the force constant in terms of the parameters  $D_e$  and  $a_i$ .

**b.** Show that in order for a function of this form to have a minimum at  $r = r_e$ ,  $a_1$  must be both the coefficient of  $x$  and the exponential parameter.

[Solution](#)

**\*13.39.** Yet another model for a diatomic potential is the Bond Order function used by Garcia and Laganá [*Mol. Phys.* 56, 621(1985)], which is given as

$$E_p(x) = -D_e \sum_{n=1}^N c_n \exp(-n\beta x).$$

Show that for  $N = 2$ , with appropriate choices for the coefficients  $c_1$  and  $c_2$ , this is identical to the Morse potential of Eq. 13.146 expressed as  $E_p = D_e(1 - e^{-\beta x})^2 - D_e$ .

[Solution](#)

**\*13.40.** The parameters for the bond order (see Problem 13.39) potential of the  $^{35}\text{Cl}^{16}\text{O}$  radical with  $N = 4$  are (in atomic units)  $c_1 = 2.691\,042$ ,  $c_2 = -2.545\,521$ ,  $c_3 = 1.017\,916$ ,  $c_4 = -0.163437$ ,  $De = 0.10302$ , and  $\beta = 1.763\,768$ . What is the vibrational frequency (in  $\text{cm}^{-1}$ ) predicted by this model? [Note that the force constant can be expressed in units of energy area $^{-1}$ .]

[Solution](#)

**\*13.41.** A model for the  $^{14}\text{N}-^{14}\text{N}-^{16}\text{O}^+$  ion assigns the following force constants for the two stretching frequencies:  $k_{12} = 1092.8\text{ N m}^{-1}$ , and  $k_{23} = 890.68\text{ N m}^{-1}$ . Use Eqs. 13.171–13.174 to calculate the two stretch frequencies obtained from the model.

[Solution](#)

**\*13.42.** The fundamental and a few successive overtones of the  $\text{H}_2^+$  molecule lie at 2191, 2064, 1941, 1821, 1705, 1591, 1479 and  $1368\text{ cm}^{-1}$ , respectively.

**a.** Starting from Eq. 13.139, derive an expression that can be used to obtain both  $\tilde{\nu}_0$  and  $x_e$  by a suitable analysis of the data.

**b.** Perform the analysis and calculate both  $\tilde{\nu}_0$  and  $x_e$ .

[Solution](#)

### Electronic Spectra

**13.43.** Sketch potential energy curves for a diatomic molecule in its ground electronic state and in an excited state, consistent with the following observations:

**a.** There is a strong  $0 \leftarrow 0$  absorption band, and strong  $0 \rightarrow 0$ ,  $1 \rightarrow 1$ , and  $2 \rightarrow 2$  emission bands.

**b.** The strongest absorption band is  $4 \leftarrow 0$ , and the strongest emission band is  $0 \rightarrow 2$ .

**c.** There is no sharp rotational fine structure in absorption, but there is a sharp emission spectrum.

**d.** The absorption spectrum shows a well-defined fine structure for the  $0 \leftarrow 0$ ,  $1 \leftarrow 0$ ,  $2 \leftarrow 0$ ,  $3 \leftarrow 0$ , and  $4 \leftarrow 0$  transitions and for the  $6 \leftarrow 0$  and  $7 \leftarrow 0$ , but not in between.

[Solution](#)

**\*13.44.** Using the data in Example 13.12 on p. 702, determine the area under the curve in a plot of  $\Delta\nu$  against  $\nu$ . Extrapolate to zero  $\Delta\nu$  to obtain  $\nu'_{\text{max}}$ , since the Birge-Sponer extrapolation shows that at that point  $\nu' = \nu'_{\text{max}}$ . A better value may be obtained by a nonlinear extrapolation. What are the values of  $\nu'$  not given in the table?

[Solution](#)

**13.45.** Calculate the dissociation energy of the hydrogen molecule ion from the vibrational energy level separations of  $\text{H}_2^+$ . The values for the transitions  $1 \leftarrow 0$ ,  $2 \leftarrow 1$ , ..., are, respectively, 2191, 2064, 1941, 1821, 1705, 1591, 1479, 1368, 1257, 1145, 1033, 918, 800, 677, 548, 411, with all values given in  $\text{cm}^{-1}$ . Use both a linear plot and a curve to obtain answers.

[Solution](#)

- 13.46.** The electronic spectra of diatomic molecules in the gas phase typically show extensive vibrational structure superimposed on the broader electronic transition. Taking the equilibrium geometry of the ground electronic state to be the zero energy, the  $\tilde{G}(v'')$  of Eq. 13.138 can be used to express the energies of the vibrational states  $v''$  (in  $\text{cm}^{-1}$ ) of this electronic state. Denoting the minimum energy of the excited electronic state as  $\tilde{T}_e$  (in  $\text{cm}^{-1}$ ), the vibrational energy levels  $v'$  of the excited state can be expressed as  $\tilde{T}_e + \tilde{G}(v')$ . Derive an expression for the frequencies  $\tilde{\nu}$  of the transitions  $v'' \rightarrow v'$  between the vibrational levels of the ground and excited electronic states. (Note that the vibrational frequencies and anharmonicity constants are not the same for the ground and excited electronic states.)

[Solution](#)

- 13.47.** An easy and reliable way to analyze the electronic spectrum of a diatomic molecule is to use the equation derived in Problem 13.46 as the model for a multiple regression analysis (several plotting packages and mathematics packages such as Mathcad can perform this task) to simultaneously identify the five unknowns,  $\tilde{T}_e$ ,  $\tilde{\nu}'_0$ ,  $\tilde{\nu}'_0 x'_e$ ,  $\tilde{\nu}''_0$ , and  $\tilde{\nu}''_0 x''_e$  [McNaught, *J. Chem. Ed.* 57, 101(1980)]. The following data are from the electronic spectrum of iodine.

$0 \rightarrow v'$	$\lambda$ (nm)	$1 \rightarrow v'$	$\lambda$ (nm)	$2 \rightarrow v'$	$\lambda$ (nm)
17	567.2	15	581.0	10	607.3
18	564.2	16	577.8	11	603.1
19	561.5	17	574.2	12	599.1
20	558.5	18	571.3	13	595.5
21	555.8	19	568.3	14	591.8
22	553.0	20	565.2	15	588.1
23	550.1	21	559.6	16	584.8
24	547.8	22	556.9	17	581.2
25	542.7	23	554.2	18	578.1
26	540.7	24	551.8	19	575.1
27	538.5	25	549.0	20	572.4

Perform a multiple regression analysis and identify the spectroscopic parameters of the ground and excited electronic states. Literature values are (in  $\text{cm}^{-1}$ )  $\tilde{T}_e = 15730$ ,  $\tilde{\nu}'_0 = 132.1$ ,  $\tilde{\nu}'_0 x'_e = 1.051$ ,  $\tilde{\nu}''_0 = 214.5$ , and  $\tilde{\nu}''_0 x''_e = 0.614$ .

[Solution](#)



**13.48.** The dissociation energy (from the zero-point level) of the ground state  $O_2(^3\Sigma_g^-)$  molecule is 5.09 eV. There exists an electronically excited  $^3\Sigma_u^-$  state of  $O_2$ , whose zero-point level lies 6.21 eV above the zero-point level of the ground state. The ground-state molecule dissociates into two ground-state O( $^3P$ ) atoms, while the  $^3\Sigma_u^-$  species dissociates into one ground-state O( $^3P$ ) atom and an O\*( $^1D$ ) atom that lies 1.97 eV above the ground state. Sketch the potential-energy curves and calculate the dissociation energy of  $O_2(^3\Sigma_u^-)$  into O + O\*( $^1D$ ).

[Solution](#)

**13.49.** The spectroscopic dissociation energy  $D_0$  is the energy required to dissociate the molecule in its ground vibrational state. This is always slightly smaller than the actual depth of the electronic potential energy because of the zero-point energy of the molecule (see Figure 13.22). Given that for HCl,  $De = 4.6173$  eV,  $\tilde{\nu}_0 = 2989$  cm $^{-1}$ , and  $\tilde{\nu}_0 x_e = 52.82$  cm $^{-1}$ , calculate the value of  $D_0$  for HCl.

[Solution](#)

**13.50.** The dissociation energy (from the zero-point level) of the ground state NO( $X^2\pi$ ) molecule is 6.6 eV. There exists an electronically excited  $B^2\Pi$  state of NO whose zero-point level lies at 5.7 eV above the zero-point level of the ground state. The ground-state molecule dissociates into ground state N( $^4S$ ) + O( $^3P$ ), while the  $B^2\Pi$  species dissociates into two ground-state atoms N( $^2D$ ) + O( $^3P$ ) that lie 3.3 eV above its ground state. Sketch the potential energy curves and calculate the dissociation energy of NO into N( $^2D$ ) + O( $^3P$ ).

[Solution](#)

**13.51.** Sodium vapor, which consists mainly of  $Na_2$  molecules, has a system of absorption bands in the green, the origin of the 0, 0 band being at 20 302.6 cm $^{-1}$ . From the spacing of the vibrational levels it can be deduced that the dissociation energy of the upper state is 0.35 eV. The dissociation of the excited  $Na_2$  gives a normal atom and an atom that emits the yellow sodium D line at 589.3 nm. Calculate the energy of dissociation of  $Na_2$  in its ground state.

[Solution](#)

For additional problems, see the books listed at the end of the problems in Chapter 12 (pp. 634-635).

### Essay Questions

**13.52.** State the laws of Lambert and Beer, and write an equation comprising the two laws.

**13.53.** Explain clearly what is meant by absorbance and transmittance, and derive a relationship between them.

**13.54.** Give an account of the fundamental origins of ultraviolet and infrared spectra.

**13.55.** Explain the selection rules for infrared spectra, with examples.

**Solutions**

**13.1.** The molar absorption coefficient of human hemoglobin (molecular weight 64 000) is  $532 \text{ cm}^{-1} \text{ mol}^{-1}$  at 430 nm. A solution of hemoglobin in a cuvette having a light path of 1 cm was found at that wavelength to have a transmittance of 76.7%. Calculate the concentration in  $\text{mol dm}^{-3}$  and in  $\text{g dm}^{-3}$ .

**Solution:**

Given:  $MW = 64\,000$ ,  $\epsilon = 532 \text{ cm}^{-1} \text{ mol}^{-1}$ ,  $\lambda = 430 \text{ nm}$ ,  $l = 1 \text{ cm}$ ,  $T = 76.7\%$

Required:  $c$  in  $\text{mol dm}^{-3}$  and in  $\text{g dm}^{-3}$

To determine the concentration of the hemoglobin solution, we use the Beer-Lambert Law, given by Eq. 13.45. This is one of the most important laws in understanding the foundation of chemical spectroscopy.

$$A = \log_{10} \frac{I_0}{I} = \epsilon cl$$

Since  $\epsilon cl$  is dimensionless, the molar absorption coefficient then has the units  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

Eq. 13.39 defines the transmittance as,

$$T \equiv \frac{I}{I_0}$$

Using the above and rearranging Eq. 13.45, we can obtain an expression that can be used to solve the problem.

$$\frac{I}{I_0} = 0.767$$

$$\frac{I_0}{I} = (0.767)^{-1} = 1.303\,780\,965$$

$$\log_{10} \frac{I_0}{I} = \epsilon c l$$

$$c = \frac{\log_{10} \frac{I_0}{I}}{\epsilon l}$$

$$c = \frac{\log_{10} 1.303\,780\,965}{(532\,\text{dm}^3\,\cancel{\text{cm}}^{-1}\,\text{mol}^{-1})(1\,\cancel{\text{cm}})}$$

$$c = 0.000\,215\,739\,\text{mol}\,\text{dm}^{-3}$$

$$\boxed{c = 2.16 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}}$$

Converting to  $\text{g}\,\text{dm}^{-3}$  we use the molecular weight given in the problem

$$c = 0.000\,215\,739\,\cancel{\text{mol}}\,\text{dm}^{-3} \times 64\,000\,\text{g}\,\cancel{\text{mol}^{-1}}$$

$$c = 13.807\,297\,2\,\text{g}\,\text{dm}^{-3}$$

$$\boxed{c = 13.8\,\text{g}\,\text{dm}^{-3}}$$

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**13.2.** A spectrophotometer has a meter that gives a reading directly proportional to the amount of light reaching the detector. When the light source is off, the reading is zero. With pure solvent in the light path, the meter reading is 78; with a 0.1 *M* solution of a solute in the same solvent, the meter reading is 55. The light path is 0.5 cm. Calculate the absorbance, the transmittance, and the molar absorption coefficient.

**Solution:**

$$\text{Given: } \frac{I_0}{I} = \frac{78}{55}, c = 0.1 \text{ M}, l = 0.5 \text{ cm}$$

Required: *A*, *T*,  $\epsilon$

To find the absorbance, we use the value given for  $\frac{I_0}{I}$  and substitute it into Eq. 13.45,

$$A = \log_{10} \frac{I_0}{I} = \epsilon cl$$

$$A = \log_{10} \frac{78}{55} = 0.151731913$$

$$\boxed{A = 0.152}$$

The transmittance is defined in Eq. 13.39 as,

$$T \equiv \frac{I}{I_0}$$

$$T = \left( \frac{55}{78} \right)$$

$$T = 0.705128205$$

$$\boxed{T = 0.705}$$

To find the molar absorption coefficient, we simply use Eq. 13.45 once more.

$$A = \varepsilon cl$$

$$\varepsilon = \frac{A}{cl}$$

$$\varepsilon = \frac{0.151731913}{0.1 \text{ mol dm}^{-3} \times 0.5 \text{ cm}}$$

$$\varepsilon = 3.034638264 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$$

$$\boxed{\varepsilon = 3.03 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}}$$

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**13.3.** The transmission of a potassium chromate solution was measured at a wavelength of 365 nm using a cell with a 1.0-cm path length. The data are as follows:

Transmission	0.357	0.303	0.194	0.124
Conc. $\times 10^4/\text{mol dm}^{-3}$	0.90	1.10	1.50	1.90

Calculate the molar Napierian absorbance and the molar decadic absorbance.

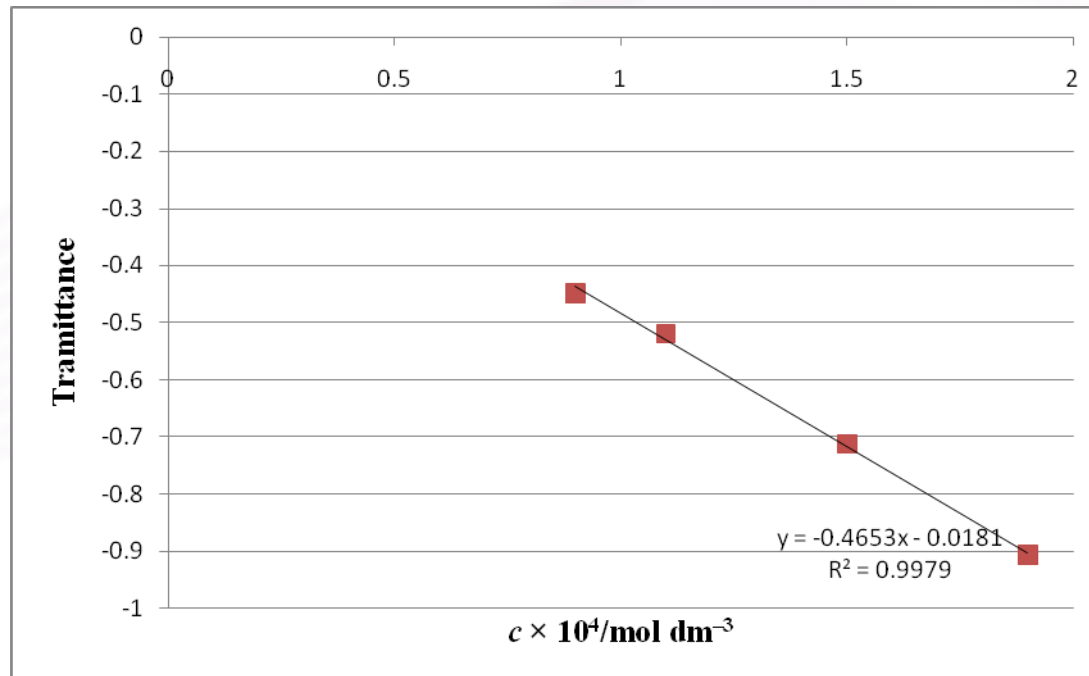
**Solution:**

Given:  $\lambda = 365 \text{ nm}$ ,  $l = 1.0 \text{ cm}$ ,  $c$

Required: Napierian and decadic absorbance

To solve this problem, we use Eq. 13.45 and form a plot of  $\log T$  against concentration.  $\log_{10} \frac{I}{I_0} = \frac{-\epsilon cl}{2.303}$

This should give a straight line with a slope of  $\frac{-\epsilon l}{2.303}$ . See the plot below.



The values used to create the plot are:

<b>Transmission</b>	0.357	0.303	0.194	0.124
<b>Conc. <math>\times 10^4/\text{mol dm}^{-3}</math></b>	0.9	1.1	1.5	1.9
<b>logT</b>	-0.44733	-0.51856	-0.7122	-0.90658

The slope of the plot obtained is  $m = -0.4653 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ .

Since  $\frac{-\epsilon l}{2.303} = -0.4653 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  we can then solve for the molar absorption coefficient.

$$\frac{\epsilon l}{2.303} = 0.4653 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$$

$$\epsilon = \frac{0.4653 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \times 2.303}{l}$$

$$l = 1.0 \text{ cm} = 0.1 \text{ dm}$$

$$\epsilon = \frac{0.4653 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \times 2.303}{0.1 \text{ dm}}$$

$$\epsilon = 10\,715.859 \text{ dm}^2 \text{ mol}^{-1}$$

$$\epsilon = 1071.5859 \text{ m}^2 \text{ mol}^{-1}$$

The decadic absorbance coefficient for a 10 M solution is then,

$$A = \epsilon c l$$

$$A = 10\,715.859 \cancel{\text{ dm}^3} \cancel{\text{ mol}^{-1}} \cancel{\text{ cm}^{-1}} \times 10 \times 10^{-6} \cancel{\text{ mol}} \cancel{\text{ dm}^{-3}} \times 1 \cancel{\text{ cm}}$$

$$A = 0.10715859$$

$$\boxed{A = 0.107}$$

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**13.4.** An aqueous solution containing 0.95 g of oxygenated myoglobin ( $M_r = 18\,800$ ) in  $100\text{ cm}^3$  gave a transmittance of 0.87 at 580 nm, with a path length of 10.0 cm. Calculate the molar absorption coefficient.

**Solution:**

Given:  $m = 0.95\text{ g}$ ,  $M_r = 18\,800$ ,  $V = 100\text{ cm}^3$ ,  $T = 0.87$ ,  $\lambda = 580\text{ nm}$ ,  $l = 10.0\text{ cm}$

Required:  $\varepsilon$

To calculate  $\varepsilon$  we use the Beer-Lambert Law in Eq. 13.45.

$$A = \log_{10} \frac{I_0}{I} = \varepsilon cl$$

The absorbance is first calculated by taking the inverse log of the transmittance.

$$A = \log_{10} T^{-1}$$

$$A = \log_{10} (0.87)^{-1}$$

$$A = 0.060\,480\,747$$

We then calculate the concentration of the hemoglobin.

$$1\text{ dm}^3 = 1000\text{ cm}^3$$

$$100\text{ cm}^3 = 0.1\text{ dm}^3$$

$$c = \frac{n}{V} = \frac{m}{M} \left( \frac{1}{V} \right)$$

$$c = \frac{0.95 \cancel{\text{ g}}}{18\,800 \cancel{\text{ g}} \text{ mol}^{-1}} \left( \frac{1}{0.1\text{ dm}^3} \right)$$

$$c = 0.000\,505\,319\text{ mol dm}^{-3}$$

$$c = 5.053\,19 \times 10^{-4}\text{ mol dm}^{-3}$$

Solving for  $\varepsilon$  we obtain,

$$\varepsilon = \frac{A}{cl}$$

$$\varepsilon = \frac{0.060\,480\,747}{5.053\,19 \times 10^{-4} \text{ mol dm}^{-3} \times 10.0 \text{ cm}}$$

$$\varepsilon = 11.968\,821\,59 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$$

$$\boxed{\varepsilon = 12.0 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}}$$

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**13.5.** A substance in aqueous solution at a concentration of  $0.01\text{ M}$  shows an optical transmittance of 28% with a path length of 2 mm. Calculate the molar absorption coefficient of the solute. What would be the transmittance in a cell 1-cm thick?

**Solution:**

Given:  $c = 0.01\text{ M}$ ,  $T = 0.28$ ,  $l = 2\text{ mm}$

Required:  $\varepsilon$ ,  $T_{l=1\text{ cm}}$

To calculate  $\varepsilon$  we use the Beer-Lambert Law in Eq. 13.45. We can solve in a similar manner to problem 13.4. The absorbance is first calculated by taking the inverse log of the transmittance.

$$A = \log_{10} \frac{I_0}{I} = \varepsilon cl$$

$$A = \log_{10} T^{-1}$$

$$A = \log_{10} (0.28)^{-1}$$

$$A = 0.552\,841\,969$$

Rearranging Eq. 13.45, we can solve for  $\varepsilon$

$$\varepsilon = \frac{A}{cl}$$

$$\varepsilon = \frac{0.552\,841\,969}{0.01\text{ mol dm}^{-3} \times 0.2\text{ cm}}$$

$$\varepsilon = 276.420\,984\,3\text{ dm}^3\text{ cm}^{-1}\text{ mol}^{-1}$$

$$\boxed{\varepsilon = 276\text{ dm}^3\text{ cm}^{-1}\text{ mol}^{-1}}$$

To determine the transmittance when the path length is 1.0 cm, we use the molar absorption coefficient obtained above and solve for the absorbance.

$$A = \varepsilon cl$$

$$A = 276.420\,984\,3\text{ dm}^3\text{ cm}^{-1}\text{ mol}^{-1} \times 0.01\text{ mol dm}^{-3} \times 1.0\text{ cm}$$

$$A = 2.764\,209\,843$$

From Eq. 13.43 we can find the transmittance,

$$\log_{10} T\% = 2 - A$$

$$\log_{10} T\% = 2 - 2.764\,209\,843$$

$$\log_{10} T\% = -0.764\,209\,843$$

$$T\% = 10^{-0.764\,209\,843}$$

$$T = 0.172\,103\,68\%$$

$$\boxed{T = 0.17\%}$$

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**13.6.** The molar absorption coefficient of hemoglobin at 430 nm is  $532 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . A solution of hemoglobin was found to have an absorbance of 0.155 at 430 nm, with a light path of 1.00 cm. Calculate the concentration.

**Solution:**

Given:  $\varepsilon = 532 \text{ cm}^{-1} \text{ mol}^{-1}$   $\lambda = 430 \text{ nm}$ ,  $l = 1.00 \text{ cm}$ ,  $A = 0.155$

Required:  $c$

This problem is similar to problem 13.1, however is much simpler to solve. By rearranging Eq. 13.45, we can obtain the concentration

$$A = \varepsilon cl$$

$$c = \frac{A}{\varepsilon l}$$

$$c = \frac{0.155}{532 \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{cm}^{-1}} \times 1.00 \cancel{\text{cm}}}$$

$$c = 0.000\,291\,353 \text{ mol dm}^{-3}$$

$$\boxed{c = 2.91 \times 10^{-4} \text{ mol dm}^{-3}}$$

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**13.7.** A  $10\ \mu\text{M}$  solution of a substance gave an absorbance of 0.1028 with a light path of 1 cm. Calculate the molar absorption coefficient. What would be the percentage light transmittance of a  $1\text{-}\mu\text{M}$  solution with the same light path?

**Solution:**

Given:  $c = 10\ \mu\text{M}$ ,  $A = 0.1028$ ,  $l = 1\text{ cm}$

Required:  $\varepsilon$ ,  $T_{c=1\ \mu\text{M}}$

To calculate  $\varepsilon$  we rearrange the Beer-Lambert Law, Eq. 13.45.

$$A = \varepsilon cl$$

$$\varepsilon = \frac{A}{cl}$$

$$\varepsilon = \frac{0.1028}{10 \times 10^{-6}\ \text{mol dm}^{-3} \times 1\text{ cm}}$$

$$\varepsilon = 10\,280\ \text{dm}^3\ \text{cm}^{-1}\ \text{mol}^{-1}$$

$$\boxed{\varepsilon = 1.028 \times 10^4\ \text{dm}^3\ \text{cm}^{-1}\ \text{mol}^{-1}}$$

To determine the transmittance when the concentration is  $1\ \mu\text{M}$ , we use the molar absorption coefficient obtained above and solve for the absorbance.

$$A = \varepsilon cl$$

$$A = 1.028 \times 10^4\ \cancel{\text{dm}^3}\ \cancel{\text{cm}^{-1}}\ \cancel{\text{mol}^{-1}} \times 10^{-6}\ \cancel{\text{mol}}\ \cancel{\text{dm}^{-3}} \times 1.0\ \cancel{\text{cm}}$$

$$A = 1.028 \times 10^{-2}$$

From Eq. 13.43 we can find the transmittance,

$$\log_{10} T\% = 2 - A$$

$$\log_{10} T\% = 2 - 1.028 \times 10^{-2}$$

$$\log_{10} T\% = 1.989\,72$$

$$T\% = 10^{1.989\,72}$$

$$T = 97.660\,737\,6\,\%$$

$$\boxed{T = 97.66\,\%}$$

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**13.8.** Two substances of biological importance,  $\text{NAD}^+$  and  $\text{NADH}$ , have equal absorption coefficients,  $1.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , at 260 nm (a wavelength at which absorption coefficients are equal is known as the *isosbestic point*<sup>6</sup>). At 340 nm,  $\text{NAD}^+$  does not absorb at all, but  $\text{NADH}$  has an absorption coefficient of  $6.22 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . A solution containing both substances had an absorbance of 0.215 at 340 nm and of 0.850 at 260 nm. Calculate the concentration of each substance.

**Solution:**

Given:  $\lambda = 260 \text{ nm}$ ;  $\epsilon_{\text{both}} = 1.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $A = 0.850$

$\lambda = 340 \text{ nm}$ ;  $\epsilon_{\text{NADH}} = 6.22 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $A = 0.215$

Required:  $c_{\text{NAD}^+}$ ,  $c_{\text{NADH}}$

Since we are told that at 340 nm,  $\text{NAD}^+$  does not absorb at all, we can find the concentration for  $\text{NADH}$  by applying the Beer-Lambert law at 340 nm. We can assume the path length,  $l = 1.00 \text{ cm}$  which is the standard value.

$$A = \epsilon cl$$

$$c = \frac{A}{\epsilon l}$$

$$c_{\text{NADH}} = \frac{0.215}{6.22 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{cm}^{-1}} \times 1.00 \cancel{\text{cm}}}$$

$$c_{\text{NADH}} = 3.45659 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\boxed{c_{\text{NADH}} = 3.46 \times 10^{-5} \text{ mol dm}^{-3}}$$

To find the concentration of  $\text{NAD}^+$ , we first calculate the absorbance of  $\text{NADH}$  at 260 nm.

$$A = \epsilon cl$$

$$A = 1.8 \times 10^4 \cancel{\text{dm}^3} \cancel{\text{cm}^{-1}} \cancel{\text{mol}^{-1}} \times 3.45659 \times 10^{-5} \cancel{\text{mol}} \cancel{\text{dm}^{-3}} \times 1.00 \cancel{\text{cm}}$$

$$A = 0.622186495$$

The remaining absorbance at 260 nm will be purely the absorbance of  $\text{NAD}^+$ ,

<sup>6</sup>From the Greek prefix *iso-*, the same, and *sbestos*, quench. This word is sometimes incorrectly written as “isobestic.”

$$A_{\text{NAD}^+} = 0.850 - 0.622\,186\,495$$

$$A_{\text{NAD}^+} = 0.227\,813\,505$$

Now we can solve for concentration in a similar manner as above.

$$c = \frac{A}{\epsilon l}$$

$$c_{\text{NAD}^+} = \frac{0.227\,813\,505}{1.80 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{cm}^{-1}} \times 1.00 \cancel{\text{cm}}}$$

$$c_{\text{NAD}^+} = 1.265\,63 \times 10^{-5} \text{ mol dm}^{-3}$$

$$c_{\text{NAD}^+} = 1.27 \times 10^{-5} \text{ mol dm}^{-3}$$

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**13.9.** The transmittance of a 0.01 *M* solution of bromine in carbon tetrachloride, with a path length of 2 mm, is 28%. Calculate the molar absorption coefficient of bromine at that wavelength. What would the percentage transmittance be in a cell 1-cm thick?

**Solution:**

Given:  $c = 0.01 \text{ M}$ ,  $T = 0.28$ ,  $l = 2 \text{ mm}$

Required:  $\varepsilon$ ,  $T_{l=1 \text{ cm}}$

This problem is parallel to problem 13.5. To calculate  $\varepsilon$  we use the Beer-Lambert Law in Eq. 13.45.

The absorbance is first calculated by taking the inverse log of the transmittance.

$$A = \log_{10} \frac{I_0}{I} = \varepsilon cl$$

$$A = \log_{10} T^{-1}$$

$$A = \log_{10} (0.28)^{-1}$$

$$A = 0.552\,841\,969$$

Rearranging Eq. 13.45, we can solve for  $\varepsilon$

$$\varepsilon = \frac{A}{cl}$$

$$\varepsilon = \frac{0.552\,841\,969}{0.01 \text{ mol dm}^{-3} \times 0.2 \text{ cm}}$$

$$\varepsilon = 276.420\,984\,3 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$$

$$\boxed{\varepsilon = 276 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}}$$

To determine the transmittance when the path length is 1.0 cm, we use the molar absorption coefficient obtained above and solve for the absorbance.

$$A = \varepsilon cl$$

$$A = 276.420\,984\,3 \cancel{\text{ dm}^3} \cancel{\text{ cm}^{-1}} \cancel{\text{ mol}^{-1}} \times 0.01 \cancel{\text{ mol}} \cancel{\text{ dm}^{-3}} \times 1.0 \cancel{\text{ cm}}$$

$$A = 2.764\,209\,843$$

From Eq. 13.43 we can find the transmittance,

$$\log_{10} T\% = 2 - A$$

$$\log_{10} T\% = 2 - 2.764\,209\,843$$

$$\log_{10} T\% = -0.764\,209\,843$$

$$T\% = 10^{-0.764\,209\,843}$$

$$T = 0.172\,103\,68\%$$

$$T = 0.17\%$$

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**13.10.** An acid HA ionizes in aqueous solution into  $\text{H}^+$  and  $\text{A}^-$  ions. At a wavelength of 430 nm HA does not absorb light, but  $\text{A}^-$  does so with an absorption coefficient of  $458 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$ . A solution of the acid at a concentration of 0.1 M was found to have a transmittance of 1.47% at 430 nm with a path length of 1 cm and at 25 °C. Calculate the dissociation constant of HA at 25 °C, and  $\Delta G^\circ$  for the dissociation process.

**Solution:**

Given:  $\lambda = 430 \text{ nm}$ ,  $\varepsilon = 458 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$ ,  $c = 0.01 \text{ M}$ ,  $T = 1.47\% = 0.0147$ ,  $l = 1 \text{ cm}$ ,  $T = 25 \text{ }^\circ\text{C}$

Required:  $K_c$ ,  $\Delta G^\circ$

To calculate the dissociation constant and Gibbs free energy, we need to recall the principles we learned in chapter 4.

The dissociation of the acid is given by,



$$K_c = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

And therefore  $K_c$  is calculated by determining the concentration of the anion  $\text{A}^-$  which is equal to  $c$ . This value is also the same concentration of  $\text{H}^+$ .

The absorbance is first calculated by taking the inverse log of the transmittance.

$$A = \log_{10} \frac{I_0}{I} = \varepsilon cl$$

$$A = \log_{10} T^{-1}$$

$$A = \log_{10} (0.0147)^{-1}$$

$$A = 1.832\ 682\ 665$$

To find  $c$ , we rearrange Eq. 13.45,



$$A = \varepsilon cl$$

$$c = \frac{A}{\varepsilon l}$$

$$c = \frac{1.832\,682\,665}{458\,\text{dm}^3\,\text{mol}^{-1}\,\cancel{\text{cm}^{-1}} \times 1.00\,\cancel{\text{cm}}}$$

$$c = 4.001\,491 \times 10^{-3}\,\text{mol dm}^{-3}$$

At equilibrium we have the following situation,

	HA	$\rightleftharpoons$	H <sup>+</sup> +	A <sup>-</sup>
$c_{\text{initial}}$	0.1 M		0	0
$c_{\text{equilibrium}}$	$0.1 - 4.001\,491 \times 10^{-3}\,\text{M}$		$4.001\,491 \times 10^{-3}\,\text{M}$	$4.001\,491 \times 10^{-3}\,\text{M}$

Solving for  $K_c$  we obtain,

$$K_c = \frac{[4.001\,491 \times 10^{-3}\,\cancel{\text{mol dm}^{-3}}][4.001\,491 \times 10^{-3}\,\text{mol dm}^{-3}]}{[1 - 4.001\,491 \times 10^{-3}\,\cancel{\text{mol dm}^{-3}}]}$$

$$K_c = 1.607\,63 \times 10^{-5}\,\text{mol dm}^{-3}$$

$$\boxed{K_c = 1.607 \times 10^{-5}\,\text{mol dm}^{-3}}$$

To find the Gibbs free energy we use Eq. 4. 27

$$\Delta G^\circ = -RT \ln K_c^\circ$$

$$\Delta G^\circ = -8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times 298.15\,\text{K} \times \ln(1.607\,63 \times 10^{-5}\,\text{mol dm}^{-3})$$

$$\Delta G^\circ = 27\,363.265\,17\,\text{J mol}^{-1}$$

$$\boxed{\Delta G^\circ = 27.4\,\text{kJ mol}^{-1}}$$

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**13.11.** In the Balmer series of the hydrogen atom, the first emission line is observed at 656.3 nm. Calculate the value of the Rydberg constant. What is the energy of the light quanta emitted during the transition?

**Solution:**

Given:  $\lambda = 656.3 \text{ nm}$ , Balmer series,

Required:  $R$ ,  $\varepsilon$

To find Rydberg's constant, we use the principles we learned in Chapter 11. We can find  $R$  using Eq. 11.50 and the fact that for the Balmer series,  $n = 3$ .  $n_1 = 2$ .

$$\bar{\nu} = \frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{656.3 \times 10^{-9} \text{ m}} = R \left( \frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$R = -\frac{35}{4} \left( \frac{1}{656.3 \times 10^{-9} \text{ m}} \right)$$

$$R = 10\,970\,592.63 \text{ m}^{-1}$$

$$\boxed{R = 1.097 \times 10^7 \text{ m}^{-1}}$$

To find the energy we use,

$$E = \frac{hc}{\lambda}$$

$$E = \frac{6.626 \times 10^{-34} \text{ J} \cancel{\text{ s}} \times 2.998 \times 10^8 \cancel{\text{ m}} \cancel{\text{ s}^{-1}}}{656.3 \times 10^{-9} \cancel{\text{ m}}}$$

$$E = 3.026\,78 \times 10^{-19} \text{ J}$$

$$\boxed{E = 3.027 \times 10^{-19} \text{ J}}$$

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**13.12.** The ground state of the Li atom has the electronic configuration  $1s^2 2s^1$ . What is its spectroscopic term? If the 2s electron is excited to the 2p state, what terms are then possible?

**Solution:**

Given: Li,  $1s^2 2s^1$

Required: spectroscopic terms for  $2s^1$  and  $2p^1$  states

The  $1s^2$  electrons form a closed shell and need not be considered.

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**13.13.** Suppose that an excited state of the carbon atom has the electronic configuration  $1s^2 2s^2 2p^1 3p^1$ . What are the possible spectroscopic terms?

**Solution:**

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**13.14.** What are the terms for the following electronic configurations?

- a. Na ( $1s^2 2s^2 2p^6 3p^1$ )
- b. Sc ( $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ )

**Solution:**

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**13.15.** What values of  $J$  may arise in the following terms?

$^1\text{P}$ ,  $^3\text{P}$ ,  $^4\text{P}$ ,  $^1\text{D}$ ,  $^2\text{D}$ ,  $^3\text{D}$ ,  $^4\text{D}$

**Solution:**

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**\*13.16.** Calculate the Landé-g-factor for a  $^2P_{1/2}$  level. What would be the anomalous Zeeman splitting for this level in a magnetic field of 4.0 T?

**Solution:**

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**\*13.17.** Calculate the spacing between the lines for a  $^3D_1 \rightarrow ^3P_0$  transition, in an anomalous Zeeman experiment with a magnetic field of 4.0 T.

**Solution:**

Given:  $^3D_1 \rightarrow ^3P_0$ ,  $B = 4.0$  T

Required:  $\Delta E$

This problem is very similar to example 13.8 given in the text, and can be solved in a similar manner.

For the  $^3P_0$  level,  $g_J = 0$ . The splitting of the line is therefore entirely due to the splitting of  $^3D_1$  level. For this level,  $g_J$  is,

$$g_J = 1 + \frac{(1 \times 2) + (1 \times 2) - (2 \times 3)}{(2 \times 2)}$$

$$g_J = \frac{1}{2}$$

It will be split into three levels with  $M_J = 1, 0, -1$ , and the separation between the levels is given by Eq. 13.88,

$$\Delta E = g_J \mu_B B$$

$$\Delta E = \frac{1}{2} \times 9.273 \times 10^{-24} \text{ J } \cancel{\text{T}} \times 4.0 \cancel{\text{T}}$$

$$\Delta E = 1.8546 \times 10^{-23} \text{ J}$$

Converting this energy level difference to the spacing in cm we get,

$$\Delta E = \frac{1.8546 \times 10^{-23} \cancel{\text{J}}}{6.626 \times 10^{-34} \cancel{\text{J}} \cancel{\text{s}} \times 2.998 \times 10^{10} \text{ cm } \cancel{\text{s}^{-1}}}$$

$$\Delta E = 0.933613656 \text{ cm}^{-1}$$

$$\boxed{\Delta E = 0.93 \text{ cm}^{-1}}$$

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**13.18.** The separation between neighboring lines in the pure rotational spectrum of  $^{35}\text{Cl}^{19}\text{F}$  is found to be  $1.023\text{ cm}^{-1}$ . Calculate the interatomic distance.

**Solution:**

Given:  $^{35}\text{Cl}^{19}\text{F}$ ,  $2B = 1.023\text{ cm}^{-1}$

Required:  $r$

Eq. 13.93 gives the relationship between interatomic distance, inertia and reduced mass.

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

To solve for interatomic distance, we first calculate the moment of inertia from Eq. 13.100 since we already have the value of the rotational constant,  $B$ .

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

$$I = \frac{h}{8\pi^2 cB}$$

$$I = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 0.5115 \text{ cm}^{-1}}$$

$$I = 5.47248 \times 10^{-46} \text{ J}$$

The reduced mass is calculated using Eq. 13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{35 \text{ g mol}^{-1} \times 19 \text{ g mol}^{-1}}{(35 + 19) \text{ g mol}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\mu = 2.04497 \times 10^{-23} \text{ g}$$

$$\mu = 2.04497 \times 10^{-26} \text{ kg}$$

Rearranging Eq. 13.93 and solving for  $r$  we obtain,

$$I = \mu r_0^2$$

$$r = \sqrt{\frac{I}{\mu}}$$

$$r = \sqrt{\frac{5.472\,48 \times 10^{-46} \text{ J}}{2.044\,97 \times 10^{-26} \text{ kg}}}$$

$$r = 1.635\,87 \times 10^{-10} \text{ m}$$

$$\boxed{r = 164 \text{ pm}}$$

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**13.19.** The lines in the pure rotational spectrum of HF are  $41.9 \text{ cm}^{-1}$  apart. Calculate the interatomic distance. Predict the separation between the lines for DF and TF.

**Solution:**

Given: HF,  $2B = 41.9 \text{ cm}^{-1}$

Required:  $r$ ,  $2B_{\text{DF}}$ ,  $2B_{\text{TF}}$

This problem can be solved in a similar manner as problem 13.18.

Eq. 13.93 gives the relationship between interatomic distance, inertia and reduced mass.

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

To solve for interatomic distance, we first calculate the moment of inertia from Eq. 13.100 since we already have the value of the rotational constant,  $B$ .

$$\tilde{B} = \frac{h}{8\pi^2 I c}$$

$$I = \frac{h}{8\pi^2 c B}$$

$$I = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \cdot 2.998 \times 10^{10} \text{ cm}^{-1} \times 20.95 \text{ cm}^{-1}}$$

$$I = 1.33612 \times 10^{-47} \text{ J}$$

The reduced mass is calculated using Eq. 13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{1 \text{ g mol}^{-1} \times 19 \text{ g mol}^{-1}}{(1+19) \text{ g mol}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\mu = 1.57755 \times 10^{-24} \text{ g}$$

$$\mu = 1.57755 \times 10^{-27} \text{ kg}$$

Rearranging Eq. 13.93 and solving for  $r$  we obtain,

$$I = \mu r_0^2$$

$$r = \sqrt{\frac{I}{\mu}}$$

$$r = \sqrt{\frac{1.33612 \times 10^{-47} \text{ J}}{1.57755 \times 10^{-27} \text{ kg}}}$$

$$r = 9.20305 \times 10^{-11} \text{ m}$$

$$\boxed{r = 92 \text{ pm}}$$

To find the separation, we take a look at Eq. 13.93 and 13.100 and notice that the separation  $B$  is inversely proportional to  $I$  and therefore, to the reduced mass  $\mu$ . The interatomic separations are assumed to be the same. The reduced mass for HF, DF and TF are in the ratio:

HF	DF	TF
$\frac{1 \times 19}{20}$	$\frac{2 \times 19}{21}$	$\frac{3 \times 19}{22}$
:	:	:
= 1	= 1.90	= 2.72

Using the ratios, the predicted separations are,

$$2B_{\text{DF}} = 41.9 \text{ cm}^{-1} \div 1.90$$

$$2B_{\text{DF}} = 21.9975 \text{ cm}^{-1}$$

$$\boxed{2B_{\text{DF}} = 22.0 \text{ cm}^{-1}}$$

$$2B_{\text{TF}} = 41.9 \text{ cm}^{-1} \div 2.72$$

$$2B_{\text{TF}} = 15.3633 \text{ cm}^{-1}$$

$$\boxed{2B_{\text{TF}} = 15.4 \text{ cm}^{-1}}$$

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**13.20.** In the microwave spectrum of  $^{12}\text{C}^{16}\text{O}$  the separation between lines has been measured to be 115270 MHz. Calculate the interatomic distance.

**Solution:**

Given:  $^{12}\text{C}^{16}\text{O}$ ,  $2B = 115\,270\text{ MHz}$

Required:  $r$

This problem can be solved in a similar manner as problem 13.18.

Eq. 13.93 gives the relationship between interatomic distance, inertia and reduced mass.

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

To solve for interatomic distance, we first calculate the moment of inertia from Eq. 13.100 since we already have the value of the rotational constant,  $B$ .

$$\tilde{B} = \frac{h}{8\pi^2 I c}$$

$$I = \frac{h}{8\pi^2 c B}$$

$$I = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \times \frac{1}{2} \times 115\,270 \times 10^6 \text{ s}^{-1}}$$

$$I = 1.456\,05 \times 10^{-46} \text{ J}$$

The reduced mass is calculated using Eq. 13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{12.000 \text{ g mol}^{-1} \times 15.995 \text{ g mol}^{-1}}{(12.000 + 15.995) \text{ g mol}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\mu = 1.138\,53 \times 10^{-23} \text{ g}$$

$$\mu = 1.138\,53 \times 10^{-26} \text{ kg}$$

Rearranging Eq. 13.93 and solving for  $r$  we obtain,

$$I = \mu r_0^2$$

$$r = \sqrt{\frac{I}{\mu}}$$

$$r = \sqrt{\frac{1.456\,05 \times 10^{-46} \text{ J}}{1.138\,53 \times 10^{-26} \text{ kg}}}$$

$$r = 1.130\,88 \times 10^{-10} \text{ m}$$

$$\boxed{r = 113 \text{ pm}}$$

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- \*13.21. The  $J = 0 \rightarrow J = 1$  line in the microwave absorption spectrum of  $^{12}\text{C}^{16}\text{O}$  and of  $^{13}\text{C}^{16}\text{O}$  was measured by Gillam et al., [*Phys. Rev.* 78, 140(1950)]. In its ground vibrational state, the former has the value  $3.842\,35\text{ cm}^{-1}$  and the latter, the value  $3.673\,37\text{ cm}^{-1}$ . Calculate
- the bond length of the  $^{12}\text{C}^{16}\text{O}$  molecule,
  - the relative atomic mass of  $^{13}\text{C}$ ,
  - the bond length of the  $^{13}\text{C}^{16}\text{O}$  molecule.

**Solution:**

Given:  $^{12}\text{C}^{16}\text{O}; \tilde{\nu}_j = 3.842\,35\text{ cm}^{-1}$ ,  $^{13}\text{C}^{16}\text{O}; \tilde{\nu}_j = 3.673\,37\text{ cm}^{-1}$

Required:  $r(^{12}\text{C}^{16}\text{O}), M_r, r(^{13}\text{C}^{16}\text{O})$

a. This problem can be solved in a similar manner as problem 13.18 since interatomic distance is the same as bond length.

Eq. 13.93 gives the relationship between interatomic distance, inertia and reduced mass.

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

First, we calculate the moment of inertia from Eq. 13.99 and Eq. 13.100. For the transition  $J = 0 \rightarrow J = 1$ ,  $\Delta \tilde{\nu} = 2B$  and therefore

$$\tilde{\nu}_j = 2(J+1)\tilde{B}$$

$$\tilde{\nu}_j = 2(J+1)\frac{h}{8\pi^2 I c}$$

$$I = \frac{2h}{8\pi^2 c \tilde{\nu}_j}$$

$$I = \frac{2 \times 6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 3.842\,35 \text{ cm}^{-1}}$$

$$I = 1.457\,01 \times 10^{-46} \text{ J s}$$

$$I = 1.457\,01 \times 10^{-46} \text{ kg m}^2$$

The reduced mass is calculated using Eq.13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{12.000 \text{ g mol}^{-1} \times 15.994\,914 \text{ g mol}^{-1}}{(12.000 + 15.994\,914) \text{ g mol}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}} \times 10^{-3} \text{ kg g}^{-1}$$

$$\mu = 1.138\,53 \times 10^{-26} \text{ kg}$$

Rearranging Eq. 13.93 and solving for  $r$  we obtain,

$$I = \mu r_0^2$$

$$r = \sqrt{\frac{I}{\mu}}$$

$$r = \sqrt{\frac{1.457\,01 \times 10^{-46} \cancel{\text{kg}} \text{ m}^2}{1.138\,53 \times 10^{-26} \cancel{\text{kg}}}}$$

$$r = 1.131\,25 \times 10^{-10} \text{ m}$$

$r = 113.1 \text{ pm} = 0.1131 \text{ nm}$

b. To find the reduced mass, we take a look at Eq. 13.93 and 13.100 and notice that the separation  $B$  is inversely proportional to the reduced mass  $\mu$ .

If  $M_r$  is the relative mass of  $^{13}\text{C}$ , and subscript 1 refers to  $^{12}\text{C}^{16}\text{O}$  and, subscript 2 refers to  $^{13}\text{C}^{16}\text{O}$ , we have,



$$\frac{B_1}{B_2} = \frac{\mu_1}{\mu_2}$$

$$\frac{3.842\,35\text{ cm}^{-1}}{3.673\,37\text{ cm}^{-1}} = \frac{12.000 \times 15.994\,914}{12.000 + 15.994\,914} \times \frac{M_r \times 15.994\,914}{M_r + 15.994\,914}$$

$$1.046\,001\,356 = 0.145\,853\,207 \times \left( \frac{M_r \times 15.994\,914}{M_r + 15.994\,914} \right)$$

$$7.171\,603\,411 = \frac{M_r \times 15.994\,914}{M_r + 15.994\,914}$$

$$7.171\,603\,411(M_r + 15.994\,914) = 15.994\,914M_r$$

$$114.709\,179\,8 = 8.823\,310\,589M_r$$

$$\boxed{M_r = 13.000\,696\,13}$$

c. This problem can be solved in a similar manner as part a.

Eq. 13.93 gives the relationship between interatomic distance, inertia and reduced mass.

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

First, we calculate the moment of inertia from Eq. 13.99 and Eq. 13.100. For the transition  $J = 0 \rightarrow J = 1$ ,  $\Delta \tilde{\nu} = 2B$  and therefore

$$\tilde{\nu}_j = 2(J+1)\tilde{B}$$

$$\tilde{\nu}_j = 2(J+1)\frac{h}{8\pi^2 Ic}$$

$$I = \frac{2h}{8\pi^2 c \tilde{\nu}_j}$$

$$I = \frac{2 \times 6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 3.673\,37 \text{ cm}^{-1} \text{ s}^{-1}}$$

$$I = 1.524\,04 \times 10^{-46} \text{ J s}$$

$$I = 1.524\,04 \times 10^{-46} \text{ kg m}^2$$

The reduced mass is calculated using Eq.13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$
$$\mu = \frac{13.003\,35\,\text{g mol}^{-1} \times 15.994\,914\,\text{g mol}^{-1}}{(13.003\,35 + 15.994\,914)\,\text{g mol}^{-1} \times 6.022 \times 10^{23}\,\text{mol}^{-1}} \times 10^{-3}\,\text{kg g}^{-1}$$
$$\mu = 1.191\,03 \times 10^{-26}\,\text{kg}$$

Rearranging Eq. 13.93 and solving for  $r$  we obtain,

$$I = \mu r_0^2$$
$$r = \sqrt{\frac{I}{\mu}}$$
$$r = \sqrt{\frac{1.524\,04 \times 10^{-46}\,\text{kg m}^2 \cancel{\text{kg m}^2}}{1.191\,03 \times 10^{-26}\,\cancel{\text{kg}}}}$$
$$r = 1.131\,19 \times 10^{-10}\,\text{m}$$

$r = 113.1\,\text{pm} = 0.1131\,\text{nm}$

Therefore, there is essentially no difference in the bond length with the  $^{13}\text{C}$  isotope.

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**13.22.** The microwave spectrum of  $^{16}\text{O}^{12}\text{C}^{32}\text{S}$  shows absorption lines separated by 12.163 GHz. That of  $^{16}\text{O}^{12}\text{C}^{34}\text{S}$  shows lines separated by 11.865 GHz. The determination of the bond distances involves solving two simultaneous quadratic equations, which is best done by successive approximations. To avoid all that labor, simply confirm that the results are consistent with  $r(\text{O}-\text{C}) = 116 \text{ pm}$  and  $r(\text{C}-\text{S}) = 156 \text{ pm}$ .

**Solution:**

Given:  $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ ;  $2B = 12.163 \text{ GHz}$ ,  $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ ,  $2B = 11.865 \text{ GHz}$

Required: confirm that the results are consistent with  $r(\text{O}-\text{C}) = 116 \text{ pm}$ ,  $r(\text{C}-\text{S}) = 156 \text{ pm}$

To confirm that the bond distances are consistent with  $r(\text{O}-\text{C}) = 116 \text{ pm}$ ,  $r(\text{C}-\text{S}) = 156 \text{ pm}$ , we can calculate and compare the moments of inertia based on the absorption line separations and the bond distances.

The  $B$  values are half the separations,

$$^{16}\text{O}^{12}\text{C}^{32}\text{S}; B = 6.0815 \times 10^9 \text{ s}^{-1}$$

$$^{16}\text{O}^{12}\text{C}^{34}\text{S}, B = 5.9325 \times 10^9 \text{ s}^{-1}$$

We can then calculate the moment of inertia from Eq. 13.100 since we already have the value of the rotational constant,  $B$ .

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

$$I = \frac{h}{8\pi^2 cB}$$

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \times 6.0815 \times 10^9 \text{ s}^{-1}}$$

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = 1.37991 \times 10^{-45} \text{ J}$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \times 5.9325 \times 10^9 \text{ s}^{-1}}$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = 1.41457 \times 10^{-45} \text{ J}$$

The moment of inertia of a linear triatomic molecule is given by Eq. 13.103

$$I = m_1 r_{12}^2 + m_3 r_{23}^2 - \frac{(m_1 r_{12} - m_3 r_{23})^2}{m}$$

We can write  $x$  for  $r_{12}$  and  $y$  for  $r_{23}$ , and  $M_1$ ,  $M_2$  and  $M_3$  for the molar masses. We then obtain the following quadratic equations,

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = \frac{1}{L} \left( M_1 x^2 + M_3 y^2 - \frac{(M_1 x - M_3 y)^2}{M} \right)$$

$$= 1.379\,91 \times 10^{-45} \text{ J} = 1.379\,91 \times 10^{-42} \text{ g m}^2$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = \frac{1}{L} \left( M_1 x^2 + M_3' y^2 - \frac{(M_1 x - M_3' y)^2}{M} \right)$$

$$= 1.414\,57 \times 10^{-45} \text{ J} = 1.414\,57 \times 10^{-42} \text{ g m}^2$$

Insertion of  $L = 6.022 \times 10^{23} \text{ mol}^{-1}$ ,  $M_1 = 16 \text{ g mol}^{-1}$ ,  $M_3 = 32 \text{ g mol}^{-1}$ ,  $M_3' = 34 \text{ g mol}^{-1}$ ,  $M = 60 \text{ g mol}^{-1}$ ,  $x = 116 \text{ pm}$ , and  $y = 156 \text{ pm}$  into the left hand side (LHS) and right hand side (RHS) of these equations gives,

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S});$$

LHS:

$$= 1.379\,91 \times 10^{-42} \text{ g m}^2$$

RHS:

$$= \frac{\left( 16 \text{ g mol}^{-1} \times (116 \text{ pm})^2 + 32 \text{ g mol}^{-1} \times (156 \text{ pm})^2 - \frac{(16 \text{ g mol}^{-1} \times 116 \text{ pm} - 32 \text{ g mol}^{-1} \times 156 \text{ pm})^2}{60 \text{ g mol}^{-1}} \right)}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= \frac{830\,139.733\,3 \text{ g pm}^2 \cancel{\text{mol}^{-1}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}} \times \left( \frac{10^{-12} \text{ m}}{\text{pm}} \right)^2$$

$$= 1.378\,51 \times 10^{-42} \text{ g m}^2$$

$$\boxed{\text{LHS} \approx \text{RHS} = 1.38 \times 10^{-42} \text{ g m}^2}$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S});$$

LHS:

$$= 1.414\,57 \times 10^{42} \text{ g m}^2$$

RHS:

$$= \frac{\left( 16 \text{ g mol}^{-1} \times (116 \text{ pm})^2 + 34 \text{ g mol}^{-1} \times (156 \text{ pm})^2 - \frac{(16 \text{ g mol}^{-1} \times 116 \text{ pm} - 34 \text{ g mol}^{-1} \times 156 \text{ pm})^2}{60 \text{ g mol}^{-1}} \right)}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= \frac{844\,574.933\,3 \text{ g pm}^2 \cancel{\text{mol}^{-1}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}} \times \left( \frac{10^{-12} \text{ m}}{\text{pm}} \right)^2$$

$$= 1.402\,48 \times 10^{42} \text{ g m}^2$$

$$\boxed{\text{LHS} \approx \text{RHS} = 1.4 \times 10^{42} \text{ g m}^2}$$

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**13.23.** The maximum potential energy that a diatomic molecule can store is  $\frac{1}{2}kx^2$ , where  $x$  is the amplitude of vibration. If the force constant  $k$  is  $1.86 \times 10^3 \text{ N m}^{-1}$ , calculate the maximum amplitude of vibration for the CO molecule in the  $v = 0$  vibrational state. Compare this to the bond length obtained in Problem 13.21. Use the value of  $\mu$  in that problem.

Solution:

Given:  $k = 1.86 \times 10^3 \text{ N m}^{-1}$ ,  $v_{\text{CO}} = 0$ , Problem 13.21

Required:  $x$ , compare with  $r$  in Problem 13.21

To solve for amplitude of vibration,  $x$ , we substitute using Eq. 13.123 and rearrange the equation given above to get,

$$\frac{1}{2}kx^2 = \frac{h}{4\pi} \sqrt{\frac{k}{\mu}}$$

$$x^2 = \frac{h}{2\pi} \sqrt{\frac{1}{k\mu}}$$

$$x = \left( \frac{h}{2\pi} \sqrt{\frac{1}{k\mu}} \right)^{\frac{1}{2}}$$

We use  $\mu = 1.19103 \times 10^{-26} \text{ kg}$  from Problem 13.21, substitute and solve to obtain,

$$x = \left( \frac{6.626 \times 10^{-34} \text{ J s}}{2\pi} \sqrt{\frac{1}{1.86 \times 10^3 \text{ N m}^{-1} \times 1.19103 \times 10^{-26} \text{ kg}}} \right)^{\frac{1}{2}}$$

$$x = \left( 2.24054 \times 10^{-23} \text{ m}^2 \right)^{\frac{1}{2}}$$

$$x = \left( 2.24054 \times 10^{-23} \text{ m}^2 \right)^{\frac{1}{2}}$$

$$x = 4.73344 \times 10^{-12} \text{ m} = 4.73344 \times 10^{-3} \text{ nm} = 0.0473344 \text{ \AA}$$

In Problem 13.21, the bond length for the CO molecule was found as  $r = 0.1131 \text{ nm}$ .  
Compared to  $x$ ,

$$\% \text{ change} = \frac{4.733\,44 \times 10^{-3} \cancel{\text{nm}}}{0.1131 \text{ nm}} \times 100\%$$

$$\% \text{ change} = 4.184\,474\,8\%$$

$$\% \text{ change} = 4.2\%$$

The extension therefore represents about a 4% change.

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- 13.24.** Consider the following molecules:  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NH}_3$ , and  $\text{SF}_6$ . Which of them will give
- a pure rotational spectrum,
  - a vibrational-rotational spectrum,
  - a pure rotational Raman spectrum,
  - a vibrational Raman spectrum?

**Solution:**

Given:  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NH}_3$ , and  $\text{SF}_6$

Required: see above

	a. pure rotational spectrum	b. vibrational-rotational spectrum	c. pure rotational Raman spectrum	d. vibrational Raman spectrum
$\text{H}_2$			✓	✓
$\text{HCl}$	✓	✓	✓	✓
$\text{CO}_2$		✓	✓	✓
$\text{CH}_4$		✓		✓
$\text{H}_2\text{O}$	✓	✓	✓	✓
$\text{CH}_3\text{Cl}$	✓	✓	✓	✓
$\text{CH}_2\text{Cl}_2$	✓	✓	✓	✓
$\text{H}_2\text{O}_2$	✓	✓	✓	✓
$\text{NH}_3$	✓	✓	✓	✓
$\text{SF}_6$		✓		✓

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**13.25.** Analysis of the vibrational-rotational spectrum of the  $\text{H}^{35}\text{Cl}$  molecule shows that its fundamental vibrational frequency  $\nu_0$  is  $2988.9\text{ cm}^{-1}$ . Calculate the force constant of the H—Cl bond.

**Solution:**

Given:  $\text{H}^{35}\text{Cl}$ ,  $\nu_0 = 2988.9\text{ cm}^{-1}$

Required:  $k$

The force constant is defined in terms of the fundamental frequency in Eq. 13.122,

$$k = 4\pi^2 \nu_0^2 \mu$$

The frequency, in terms of inverse seconds is given by,

$$\nu = \nu_0 c$$

$$\nu = 2.998 \times 10^{10} \cancel{\text{cm}} \text{ s}^{-1} \times 2988.9 \cancel{\text{cm}^{-1}}$$

$$\nu = 8.9907 \times 10^{13} \text{ s}^{-1}$$

The reduced mass is calculated using Eq. 13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{34.96885 \text{ g mol}^{-1} \times 1.007825 \text{ g mol}^{-1}}{(34.96885 + 1.007825) \text{ g mol}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}} \times 10^{-3} \text{ kg g}^{-1}$$

$$\mu = 1.62669 \times 10^{-27} \text{ kg}$$

Solving for  $k$  we get,

$$k = 4\pi^2 \nu_0^2 \mu$$

$$k = 4\pi^2 (8.9907 \times 10^{13} \text{ s}^{-1})^2 \times 1.62669 \times 10^{-27} \text{ kg}$$

$$k = 519.1007608 \text{ kg s}^{-2}$$

$$\boxed{k = 519.10 \text{ kg s}^{-2}}$$

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**13.26.** A few transitions in the P and R branches of the infrared spectrum of  $\text{H}^{35}\text{Cl}$  spectrum are identified below.

$J''$	0	1	2	3	4	5	6
P ( $\text{cm}^{-1}$ )		2865.10	2843.62	2821.56	2798.94	2775.76	2752.04
R ( $\text{cm}^{-1}$ )	2906.24	2925.90	2944.90	2963.29	2981.00	2998.04	

Using Eqs. 13.134 or 13.135 as appropriate, calculate  $\tilde{\nu}_0$  and the rotational constant  $\tilde{B}$ .

**Solution:**

Given: table above

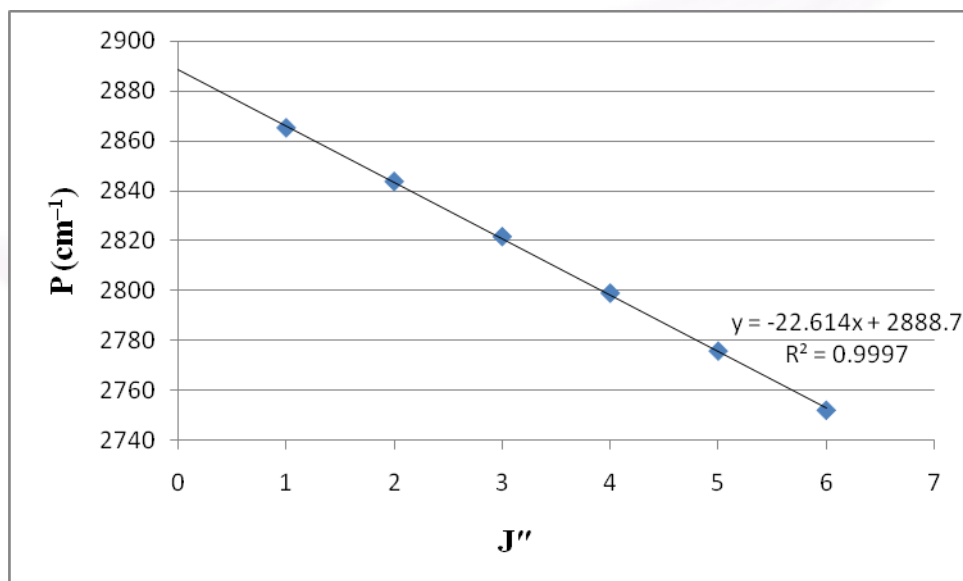
Required:  $\tilde{\nu}_0$ ,  $\tilde{B}$ .

Equations 13.135 and 13.136,

$$\tilde{\nu} = \tilde{\nu}_0 + 2(J''+1)\tilde{B} = \tilde{\nu}_0 + 2J'\tilde{B} \quad \text{and} \quad \tilde{\nu} = \tilde{\nu}_0 - 2(J'+1)\tilde{B} = \tilde{\nu}_0 - 2J''\tilde{B},$$

Both show that a plot of the observed frequencies  $\tilde{\nu}$  as a function of  $J''$  will be a straight line with slope  $= \pm 2\tilde{B}$  and intercept  $\tilde{\nu}_0$ .

A linear regression of the values in the P branch gives the following plot.



This gives,

$$\tilde{\nu} = 2888.70 - 22.614J''$$

From which we obtain the fundamental vibrational frequency as,

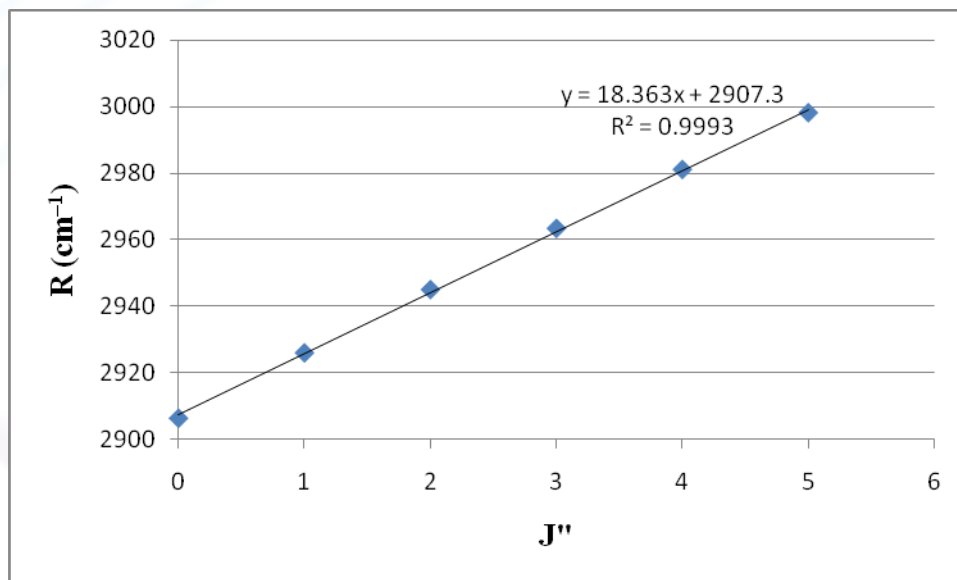
$$\tilde{\nu}_0 = 2888.70 \text{ cm}^{-1}$$

And the value  $\tilde{B}$  as,

$$\tilde{B} = \frac{-22.614}{\pm 2}$$

$$\tilde{B} = 11.307 \text{ cm}^{-1}$$

Similarly, we can perform a linear regression of the values in the B branch to give the following results.



$$\tilde{\nu} = 2907.3 - 18.363J''$$

From which we obtain the fundamental vibrational frequency as,

$$\tilde{\nu}_0 = 2907.3 \text{ cm}^{-1}$$

And the value  $\tilde{B}$  as,

$$\tilde{B} = \frac{-18.363}{\pm 2}$$

$$\tilde{B} = 9.1815 \text{ cm}^{-1}$$

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**13.27.** Comparison of the results of Problem 13.26 to experimental values for  $\text{H}^{35}\text{Cl}$  ( $\tilde{\nu}_0 = 2990 \text{ cm}^{-1}$ , and  $\tilde{B} = 10.59 \text{ cm}^{-1}$ ) shows that Eqs. 13.134 and 13.135 do not accurately relate the observed transitions to the rotational quantum numbers. Much of the error results from not taking the anharmonicity of the potential energy curve into account. Using the definition (see Eq. 13.138)  $T_{v,J} = (v + \frac{1}{2})\tilde{\nu}_0 - (v + \frac{1}{2})^2 \tilde{\nu}_0 x_e + J(J+1)\tilde{B}$ , derive a more accurate expression for  $\Delta T_{v,J}$  for the  $v'' = 0 \rightarrow v' = 1$  transitions of a diatomic molecule. [Even this is an approximate treatment because we are ignoring the coupling of rotations with vibrations.]

**Solution:**

Given  $T_{v,J} = (v + \frac{1}{2})\tilde{\nu}_0 - (v + \frac{1}{2})^2 \tilde{\nu}_0 x_e + J(J+1)\tilde{B}$ ,

Required: expression for  $\Delta T_{v,J}$  for the  $v'' = 0 \rightarrow v' = 1$  transitions of a diatomic molecule

To derive a more accurate expression for  $\Delta T_{v,J}$ , we first write the following expressions for  $v = 0$  and  $v = 1$ ,

$$T_{0,J''} = \frac{1}{2}\tilde{\nu}_0 - \frac{1}{4}\tilde{\nu}_0 x_e + J''(J''+1)\tilde{B}$$

$$T_{1,J'} = \frac{3}{2}\tilde{\nu}_0 - \frac{9}{4}\tilde{\nu}_0 x_e + J'(J'+1)\tilde{B}$$

This gives,

$$\Delta T_{0,J'' \rightarrow 1,J'} = T_{1,J'} - T_{0,J''}$$

$$\Delta T_{0,J'' \rightarrow 1,J'} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e + \tilde{B}(J'(J'+1) - J''(J''+1))$$

For  $\Delta J = J' - J'' = -1$  (the *P* branch), this reduces to,

$$\boxed{\tilde{\nu} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e - 2\tilde{B}J''}$$

For  $\Delta J = J' - J'' = +1$  (the *R* branch), this reduces to,

$$\boxed{\tilde{\nu} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e + 2\tilde{B}J''}$$

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**13.28.** From the results of Problems 13.26 and 13.27 and the experimental value of  $\tilde{\nu}_0$  for  $\text{H}^{35}\text{Cl}$  given in Problem 13.27, estimate the value of the anharmonicity constant  $x_e$ . Use the average of the P and R branch values for  $\tilde{\nu}_0$  from Problem 13.26.

**Solution:**

Given: Problem 13.26, Problem 13.27

Required:  $x_e$

First we take the average of the P and R branch values for  $\tilde{\nu}_0$  from Problem 13.26 to get,

$$\tilde{\nu}_0 = \frac{1}{2}(2\,888.70\text{ cm}^{-1} + 2\,907.3\text{ cm}^{-1})$$

$$\tilde{\nu}_0 = 2\,898\text{ cm}^{-1}$$

The more accurate treatment of Problem 13.27 shows that this is actually the value of  $\tilde{\nu}_0 - 2\tilde{\nu}_0 x_e$ .

Therefore we can equate the two and solve for  $x_e$

$$\tilde{\nu} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e$$

$$2990\text{ cm}^{-1} = 2\,898\text{ cm}^{-1} - 2 \times 2\,898\text{ cm}^{-1} x_e$$

$$x_e = 0.015\,873\,016\text{ cm}^{-1}$$

$$\boxed{x_e = 1.587 \times 10^{-2}\text{ cm}^{-1}}$$

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**13.29.** The vibrational Raman spectrum of  $^{35}\text{Cl}_2$  shows series of Stokes and anti-Stokes lines; the separation between the lines in each of the two series is  $0.9752\text{ cm}^{-1}$ . Estimate the bond length in  $\text{Cl}_2$ .

**Solution:**

Given:  $4B = 0.9752\text{ cm}^{-1}$

Required:  $r$

From Figure 13.27, we know that the separation is  $4B$ . Therefore the value of  $B$  is,

$$B = \frac{1}{4} \times 0.9752\text{ cm}^{-1}$$

$$B = 0.2438\text{ cm}^{-1}$$

This problem can be solved in a similar manner as problem 13.18.

Eq. 13.93 gives the relationship between interatomic distance, inertia and reduced mass.

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

We calculate the moment of inertia from Eq. 13.100

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

$$I = \frac{h}{8\pi^2 cB}$$

$$I = \frac{6.626 \times 10^{-34}\text{ J s}}{8\pi^2 \times 0.2438\text{ cm}^{-1} \times 2.998 \times 10^{10}\text{ cm s}^{-1}}$$

$$I = 1.14814 \times 10^{-45}\text{ J}$$

The reduced mass is calculated using Eq.13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{35 \text{ g mol}^{-1} \times 35 \text{ g mol}^{-1}}{(35 + 35) \text{ g mol}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\mu = 2.906 01 \times 10^{-26} \text{ kg}$$

Rearranging Eq. 13.93 and solving for  $r$  we obtain,

$$I = \mu r_0^2$$

$$r = \sqrt{\frac{I}{\mu}}$$

$$r = \sqrt{\frac{1.148 14 \times 10^{-45} \text{ J}}{2.906 01 \times 10^{-26} \text{ kg}}}$$

$$r = 1.987 69 \times 10^{-10} \text{ m}$$

$$\boxed{r = 199 \text{ pm}}$$

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**13.30.** The dissociation energy of  $\text{H}_2$  is  $432.0 \text{ kJ mol}^{-1}$  and the fundamental vibrational frequency of the molecule is  $1.257 \times 10^{14} \text{ s}^{-1}$ . Calculate the classical dissociation energy. Estimate the zero-point energies of HD and  $\text{D}_2$  and their dissociation energies.

**Solution:**

Given:  $E_p = 432.0 \text{ kJ mol}^{-1}$ ,  $\nu_0 = 1.257 \times 10^{14} \text{ s}^{-1}$

Required: classical dissociation  $E$ , estimated zero point  $E$ , dissociation  $E$ ,

The zero point energy of  $\text{H}_2$  is given by

$$E = \frac{1}{2} h \nu_0$$

$$E = \frac{1}{2} \times 6.626 \times 10^{-34} \text{ J s} \times 1.257 \times 10^{14} \text{ s}^{-1}$$

$$E = 4.16444 \times 10^{-20} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$E = 25.0782637 \text{ kJ mol}^{-1}$$

$$\boxed{E = 25.08 \text{ kJ mol}^{-1}}$$

To find the classical dissociation energy, we add the zero point energy to the dissociation energy given above.

$$E = 25.08 \text{ kJ mol}^{-1} + 432.0 \text{ kJ mol}^{-1}$$

$$\boxed{E = 457.08 \text{ kJ mol}^{-1}}$$

The reduced masses of  $\text{H}_2$ , HD and  $\text{D}_2$  are in the ratio,

$\text{H}_2$	$\text{HD}$	$\text{D}_2$
$\frac{1 \times 1}{1+1} :$	$\frac{1 \times 2}{1+2} :$	$\frac{2 \times 2}{2+2}$
$\frac{1}{2} :$	$\frac{2}{3} :$	$1$
$= 1 :$	$\frac{4}{3} :$	$2$

From Eq. 13.123,

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

we know that frequency is inversely related to  $\sqrt{\mu}$ , therefore the estimated  $\nu_0$  for HD and  $\text{D}_2$  are,

$$\nu_0(\text{HD}) = 1.257 \times 10^{14} \text{ s}^{-1} \div \sqrt{\frac{4}{3}}$$

$$\nu_0(\text{HD}) = 1.088\,59 \times 10^{14} \text{ s}^{-1}$$

$$\nu_0(\text{D}_2) = 1.257 \times 10^{14} \text{ s}^{-1} \div \sqrt{2}$$

$$\nu_0(\text{D}_2) = 8.888\,33 \times 10^{13} \text{ s}^{-1}$$

Therefore,

$$E(\text{HD}) = \frac{1}{2} \times 6.626 \times 10^{-34} \text{ J } \cancel{\text{ s }} \times 1.088\,59 \times 10^{14} \cancel{\text{ s }^{-1}}$$

$$E(\text{HD}) = 3.606\,51 \times 10^{-20} \cancel{\text{ s }} \times 10^{-3} \frac{\text{kJ}}{\cancel{\text{ s }}} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$E(\text{HD}) = 21.718\,413\,45 \text{ kJ mol}^{-1}$$

and

$$E(\text{D}_2) = \frac{1}{2} \times 6.626 \times 10^{-34} \text{ J } \cancel{\text{ s }} \times 8.888\,33 \times 10^{13} \cancel{\text{ s }^{-1}}$$

$$E(\text{D}_2) = 2.944\,7 \times 10^{-20} \cancel{\text{ s }} \times 10^{-3} \frac{\text{kJ}}{\cancel{\text{ s }}} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$E(\text{D}_2) = 17.733\,010\,32 \text{ kJ mol}^{-1}$$

The estimated dissociation energies are therefore the difference between the dissociation energies above and the classical dissociation energy,

HD;

$$E = 457.08 \text{ kJ mol}^{-1} - 21.718\,413\,45 \text{ kJ mol}^{-1}$$

$$E = 435.361\,586\,6 \text{ kJ mol}^{-1}$$

$$\boxed{E = 435.36 \text{ kJ mol}^{-1}}$$

D<sub>2</sub>;

$$E = 457.08 \text{ kJ mol}^{-1} - 17.733\,010\,32 \text{ kJ mol}^{-1}$$

$$E = 439.346\,989\,7 \text{ kJ mol}^{-1}$$

$$\boxed{E = 439.35 \text{ kJ mol}^{-1}}$$

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**13.31.** A molecule  $AB_2$  is known to be linear but it is not known whether it is  $B-A-B$  or  $A-B-B$ . Its infrared spectrum is found to show bands corresponding to three normal modes of vibration. Which is the structure?

**Solution:**

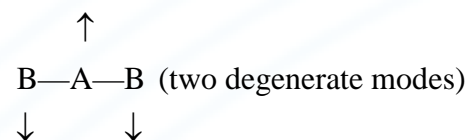
Given:  $AB_2$ , three normal modes of vibration in IR spectrum

Required: structure

The symmetric molecule,  $B-A-B$ , only has two modes that are active in the infrared region:

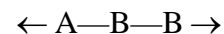


and

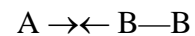


The symmetric stretch is inactive.

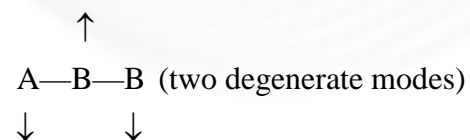
The unsymmetrical molecule,  $A-B-B$  have three modes that are active in the infrared region:



and



and



Therefore the structure of the molecule is  $A-B-B$ .

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**13.32.** The frequency of the O—H stretching vibration in  $\text{CH}_3\text{OH}$  is  $3300\text{ cm}^{-1}$ . Estimate the frequency of the O—D stretching vibration in  $\text{CH}_3\text{OD}$ .

**Solution:**

Given:  $\tilde{\nu}_{\text{O-H}} = 3\,300\text{ cm}^{-1}$

Required:  $\tilde{\nu}_{\text{O-D}}$

To calculate the frequency of the O—D stretching vibration, we rely on Eq. 13.123 which

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

which shows that the frequency is inversely related to  $\sqrt{\mu}$ .

The reduced masses are calculated using Eq. 13.94, and are in the following ratio

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu_{\text{OH}} = \frac{1\text{ g mol}^{-1} \times 16\text{ g mol}^{-1}}{(1+16)\text{ g mol}^{-1} \times 6.022 \times 10^{23}\text{ mol}^{-1}} = \frac{1 \times 16}{17L}$$

$$\mu_{\text{OD}} = \frac{2\text{ g mol}^{-1} \times 16\text{ g mol}^{-1}}{(2+16)\text{ g mol}^{-1} \times 6.022 \times 10^{23}\text{ mol}^{-1}} = \frac{2 \times 16}{18L}$$

$$\frac{\mu_{\text{OD}}}{\mu_{\text{OH}}} = \frac{2 \times \cancel{16}}{18\cancel{L}} \times \frac{17\cancel{L}}{1 \times \cancel{16}} = \frac{17}{9}$$

The force constants are the same, and therefore the frequency of the O—D stretching vibration is given by,

$$\tilde{\nu}_{\text{OD}} = \tilde{\nu}_{\text{OH}} \div \sqrt{\frac{17}{9}}$$

$$\tilde{\nu}_{\text{OD}} = 3\,300\text{ cm}^{-1} \div \sqrt{\frac{17}{9}}$$

$$\tilde{\nu}_{\text{OD}} = 2\,401.102\,688\text{ cm}^{-1}$$

$$\boxed{\tilde{\nu}_{\text{OD}} = 2\,401\text{ cm}^{-1}}$$

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**13.33.** The spectroscopic constants for the OH radical are  $\tilde{\nu}_0 = 3737.76 \text{ cm}^{-1}$ ,  $\tilde{\nu}_0 x_e = 84.8813 \text{ cm}^{-1}$ ,  $\tilde{B} = 18.9108 \text{ cm}^{-1}$ . Predict the frequencies at which (a) the P branch transitions ending in, and (b) the R branch beginning in,  $J = 0, 1, 2$  will be observed.

**Solution:**

Given:  $\tilde{\nu}_0 = 3737.76 \text{ cm}^{-1}$ ,  $\tilde{\nu}_0 x_e = 84.8813 \text{ cm}^{-1}$ ,  $\tilde{B} = 18.9108 \text{ cm}^{-1}$

Required: for the P branch and R branch;  $\tilde{\nu}$  for  $J = 0, 1, 2$

a. In problem 13.27, we derived an equation for the P branch transitions, given by,

$$\tilde{\nu} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e - 2\tilde{B}J''$$

For this situation the equation becomes,

$$\tilde{\nu} = 3737.76 \text{ cm}^{-1} - 2 \times 84.8813 \text{ cm}^{-1} - 2 \times 18.9108 \text{ cm}^{-1} \times J''$$

The frequencies are then calculated by substituting the values of  $J''$  into the equation.

$J''$	0	1	2
$\tilde{\nu} (\text{cm}^{-1})$	3 567.997	3 530.176	3 492.354

b. For the R branch transitions, we use the second equation derived in problem 13.27,

$$\tilde{\nu} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e + 2\tilde{B}J''$$

$$\tilde{\nu} = 3737.76 \text{ cm}^{-1} - 2 \times 84.8813 \text{ cm}^{-1} + 2 \times 18.9108 \text{ cm}^{-1} \times J''$$

$J''$	0	1	2
$\tilde{\nu} (\text{cm}^{-1})$	3 567.997	3 605.819	3 643.641

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**13.34.** Irradiation of acetylene with mercury radiation at 435.83 nm gives rise to a Raman line at 476.85 nm. Calculate the vibrational frequency that corresponds to this shift.

**Solution:**

Given:  $\lambda_0 = 435.83 \text{ nm}$ ,  $\lambda_1 = 476.85 \text{ nm}$

Required:  $\tilde{\nu}$

To calculate the vibrational frequency that corresponds to the shift, we first calculate the wavenumbers that correspond to each wavelength.

435.83 nm;

$$\tilde{\nu} = \frac{1}{435.83 \times 10^{-9} \text{ m}}$$

$$\tilde{\nu} = 2\,294\,472.615 \text{ m}^{-1} = 22\,944.726\,15 \text{ cm}^{-1}$$

476.85 nm;

$$\tilde{\nu} = \frac{1}{476.85 \times 10^{-9} \text{ m}}$$

$$\tilde{\nu} = 2\,097\,095.523 \text{ m}^{-1} = 20\,970.955\,23 \text{ cm}^{-1}$$

The frequency that corresponds to the vibration in the  $\text{C}_2\text{H}_2$  molecule, (ie the C-C stretch) is the difference of the two,

$$\tilde{\nu} = 22\,944.726\,15 \text{ cm}^{-1} - 20\,970.955\,23 \text{ cm}^{-1}$$

$$\tilde{\nu} = 1\,973.770\,928 \text{ cm}^{-1}$$

$$\boxed{\tilde{\nu} = 1\,973.8 \text{ cm}^{-1}}$$

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**13.35.** The fundamental vibrational frequency of  $\text{H}^{127}\text{I}$  is  $2309.5 \text{ cm}^{-1}$ . Calculate the force constant of the bond.

**Solution:**

Given:  $\text{H}^{127}\text{I}$ ,  $\nu_0 = 2\,309.5 \text{ cm}^{-1}$

Required:  $k$

This problem can be solved in a similar manner as problem 13.25.

The force constant is defined in terms of the fundamental frequency in Eq. 13.122,

$$k = 4\pi^2 \nu_0^2 \mu$$

The frequency, in terms of inverse seconds is given by,

$$\nu = \nu_0 c$$

$$\nu = 2.998 \times 10^{10} \cancel{\text{cm}} \text{ s}^{-1} \times 2\,309.5 \cancel{\text{cm}^{-1}}$$

$$\nu = 6.923\,88 \times 10^{13} \text{ s}^{-1}$$

The reduced mass is calculated using Eq. 13.94,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{126.9 \text{ g mol}^{-1} \times 1.007\,825 \text{ g mol}^{-1}}{(126.9 + 1.007\,825) \text{ g mol}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}} \times 10^{-3} \text{ kg g}^{-1}$$

$$\mu = 1.660\,39 \times 10^{-27} \text{ kg}$$

Solving for  $k$  we get,

$$k = 4\pi^2 \nu_0^2 \mu$$

$$k = 4\pi^2 (6.923\,88 \times 10^{13} \text{ s}^{-1})^2 \times 1.660\,39 \times 10^{-27} \text{ kg}$$

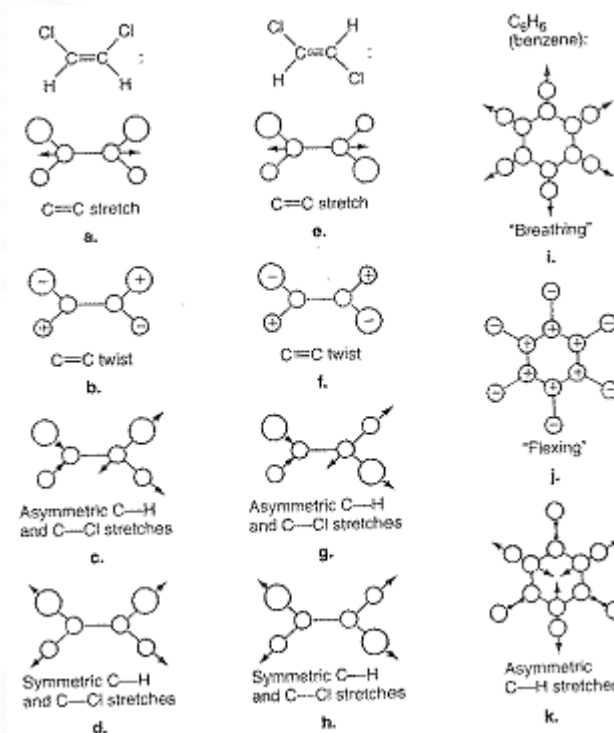
$$k = 314.244\,591 \text{ kg s}^{-2}$$

$$\boxed{k = 314.24 \text{ kg s}^{-2}}$$

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\*13.36. The following are some normal modes of vibration for several molecules:



In each case, determine the point group and refer to Appendix E on p. 1028 to determine whether the vibration is active in the infrared and in the Raman spectrum. Then check your conclusions by reference to the appendix to this chapter (p. 707).

**Solution:**

Given: image above

Required: determine point group, activity of vibration

*cis*-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>: C<sub>2v</sub> point group

		<b>Infrared</b>	<b>Raman</b>
a.	$a_1$	active	active
b.	$b_1$	inactive	active
c.	$a_2$	active	active
d.	$a_1$	active	active

*trans*-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>: C<sub>2h</sub> point group

		<b>Infrared</b>	<b>Raman</b>
e.	$a_g$	inactive	active
f.	$a_u$	active	inactive
g.	$b_u$	active	inactive
h.	$a_g$	inactive	active

Benzene: D<sub>6h</sub> point group

		<b>Infrared</b>	<b>Raman</b>
i.	$a_{1g}$	inactive	active
j.	$a_{2u}$	active	inactive
k.	$b_{1u}$	inactive	inactive

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**\*13.37.** Prove that the force constant  $k$  corresponding to the Morse potential function (Eq. 13.146) at small bond extensions is

$$k = 2D_e a^2$$

Calculate the vibration frequency  $\nu_0$  on the basis of the following Morse parameters for  $\text{H}^{35}\text{Cl}$ :

$$D_e = 4.67 \text{ eV}$$

$$a = 1.85 \times 10^8 \text{ cm}^{-1}$$

**Solution:**

Given: Morse potential,  $\text{H}^{35}\text{Cl}$ ,  $D_e = 4.67 \text{ eV}$ ,  $a = 1.85 \times 10^8 \text{ cm}^{-1}$

Required: proof,  $\nu_0$

The Morse potential function is given by Eq. 13.146

$$E_p = D_e (1 - e^{-ax})^2$$

At small  $x$  values the exponential may be expanded to  $1 - ax$ , and the potential energy will therefore be given by,

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**\*13.38.** The Morse function is only one of several models used to describe the behavior of the potential energy of diatomic molecules. A popular and very accurate model introduced by Murrell and Sorbie [*J. Chem. Soc., Faraday Trans. 2*, 70, 1552(1974)] is the so-called “Extended Rydberg function,” which is written as

$$E_p(x) = -D_e(1 + a_1x + a_2x^2 + a_3x^3)e^{-a_1x},$$

where  $x = r - r_e$ , as in the case of the Morse potential of Eq. 13.146, and the  $a_i$  are constants for a given molecule.

- a. Derive an expression for the force constant in terms of the parameters  $D_e$  and  $a_i$ .
- b. Show that in order for a function of this form to have a minimum at  $r = r_e$ ,  $a_1$  must be both the coefficient of  $x$  and the exponential parameter.

**Solution:**

Given: Extended Rydberg function

Required: expression for  $k$ , proof

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**\*13.39.** Yet another model for a diatomic potential is the Bond Order function used by Garcia and Laganá [*Mol. Phys.* 56, 621(1985)], which is given as

$$E_p(x) = -D_e \sum_{n=1}^N c_n \exp(-n\beta x).$$

Show that for  $N = 2$ , with appropriate choices for the coefficients  $c_1$  and  $c_2$ , this is identical to the Morse potential of Eq. 13.146 expressed as  $E_p = D_e(1 - e^{-\beta x})^2 - D_e$ .

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**\*13.40.** The parameters for the bond order (see Problem 13.39) potential of the  $^{35}\text{Cl}^{16}\text{O}$  radical with  $N = 4$  are (in atomic units)  $c_1 = 2.691\,042$ ,  $c_2 = -2.545\,521$ ,  $c_3 = 1.017\,916$ ,  $c_4 = -0.163437$ ,  $De = 0.10302$ , and  $\beta = 1.763\,768$ . What is the vibrational frequency (in  $\text{cm}^{-1}$ ) predicted by this model? [Note that the force constant can be expressed in units of energy area $^{-1}$ .]

Solution:

Given:

Required:

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**\*13.41.** A model for the  $^{14}\text{N}-^{14}\text{N}-^{16}\text{O}^+$  ion assigns the following force constants for the two stretching frequencies:  $k_{12} = 1092.8 \text{ N m}^{-1}$ , and  $k_{23} = 890.68 \text{ N m}^{-1}$ . Use Eqs. 13.171–13.174 to calculate the two stretch frequencies obtained from the model.

**Solution:**

Given:  $k_{12} = 1\,092.8 \text{ N m}^{-1}$ , and  $k_{23} = 890.68 \text{ N m}^{-1}$

Required:  $\tilde{\nu}_1, \tilde{\nu}_2$

To solve for the stretching frequencies, we need to solve the quadratic equation given by Eq. 13.171. For the molar masses, we use

$$m_1 = m_2 = \frac{14.00 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \text{ and } m_3 = \frac{16.00 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\lambda^2 - \left( \frac{m_1 + m_2}{m_1 m_2} k_{12} + \frac{m_2 + m_3}{m_2 m_3} k_{23} \right) \lambda + \frac{k_{12} k_{23} (m_1 + m_2 + m_3)}{m_1 m_2 m_3} = 0$$

$$\lambda^2 - (1.658\,47 \times 10^{29}) \lambda + (4.952\,45 \times 10^{57}) = 0$$

This resembles Eq. 13.172,  $\lambda^2 - b\lambda + c = 0$ , and therefore the solutions are obtained by solving Eq. 13.173 and 13.174.



$$\lambda^2 - (1.658\,47 \times 10^{29})\lambda + (4.952\,45 \times 10^{57}) = 0$$

$$\lambda_1 = \frac{b - \sqrt{b^2 - 4c}}{2}$$

$$\lambda = \frac{1.658\,47 \times 10^{29} - \sqrt{(1.658\,47 \times 10^{29})^2 - 4 \times 4.952\,45 \times 10^{57}}}{2}$$

$$\lambda_1 = 3.906\,18 \times 10^{28} \text{ s}^{-2}$$

$$\lambda_2 = \frac{b + \sqrt{b^2 - 4c}}{2}$$

$$\lambda = \frac{1.658\,47 \times 10^{29} + \sqrt{(1.658\,47 \times 10^{29})^2 - 4 \times 4.952\,45 \times 10^{57}}}{2}$$

$$\lambda_2 = 1.267\,85 \times 10^{29} \text{ s}^{-2}$$

We then calculate the stretching frequencies from,

$$\nu = \frac{\sqrt{\lambda}}{2\pi c}$$

$$\nu_1 = \frac{\sqrt{3.906\,18 \times 10^{28} \text{ s}^{-2}}}{2\pi \times 2.998 \times 10^{10} \text{ cm s}^{-1}}$$

$$\nu_1 = 1\,049.215\,077 \text{ cm}^{-1}$$

$$\boxed{\nu_1 = 1\,049.2 \text{ cm}^{-1}}$$

$$\nu_2 = \frac{\sqrt{1.267\,85 \times 10^{29} \text{ s}^{-2}}}{2\pi \times 2.998 \times 10^{10} \text{ cm s}^{-1}}$$

$$\nu_2 = 1\,890.265\,202 \text{ cm}^{-1}$$

$$\boxed{\nu_2 = 1\,890.3 \text{ cm}^{-1}}$$

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**\*13.42.** The fundamental and a few successive overtones of the  $\text{H}_2^+$  molecule lie at 2191, 2064, 1941, 1821, 1705, 1591, 1479 and 1368  $\text{cm}^{-1}$ , respectively.

- Starting from Eq. 13.139, derive an expression that can be used to obtain both  $\tilde{\nu}_0$  and  $x_e$  by a suitable analysis of the data.
- Perform the analysis and calculate both  $\tilde{\nu}_0$  and  $x_e$ .

**Solution:**

Given:  $\nu$

Required: expression for  $\tilde{\nu}_0$  and  $x$ , calculate  $\tilde{\nu}_0$  and  $x_e$

- a. Eq. 13.139 is given by

$$G(\nu) = \tilde{\nu}_0 \left[ 1 - x_e \left( \nu + \frac{1}{2} \right) \right] \left( \nu + \frac{1}{2} \right)$$

Therefore, for a transition,  $\nu'' \rightarrow \nu'$ , we can write,

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 \left[ 1 - x_e \left( \nu' + \frac{1}{2} \right) \right] \left( \nu' + \frac{1}{2} \right) - \tilde{\nu}_0 \left[ 1 - x_e \left( \nu'' + \frac{1}{2} \right) \right] \left( \nu'' + \frac{1}{2} \right)$$

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 \left[ \left( \nu' + \frac{1}{2} \right) - x_e \left( \nu' + \frac{1}{2} \right)^2 - \left( \nu'' + \frac{1}{2} \right) + x_e \left( \nu'' + \frac{1}{2} \right)^2 \right]$$

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 \left[ \cancel{\nu'} - \cancel{\frac{1}{2}} - x_e \left( \nu' + \frac{1}{2} \right)^2 - \cancel{\nu''} + \cancel{\frac{1}{2}} + x_e \left( \nu'' + \frac{1}{2} \right)^2 \right]$$

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 \left[ \nu' - \nu'' - x_e \left( \nu' + \frac{1}{2} \right)^2 + x_e \left( \nu'' + \frac{1}{2} \right)^2 \right]$$

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 \left[ \nu' - \nu'' - x_e \left( \nu'^2 + \nu' + \frac{1}{4} \right) + x_e \left( \nu''^2 + \nu'' + \frac{1}{4} \right) \right]$$

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 \left[ \nu' - \nu'' + x_e \left( \nu'^2 + \nu' - \cancel{\frac{1}{4}} - \nu''^2 - \nu'' + \cancel{\frac{1}{4}} \right) \right]$$

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 \left[ \nu' - \nu'' + x_e \left( \nu'^2 - \nu''^2 + \nu' - \nu'' \right) \right]$$

$$\Delta \tilde{G}_{\nu'} = \tilde{\nu}_0 (\nu' - \nu'') - \tilde{\nu}_0 x_e \left[ (\nu'^2 - \nu''^2) + (\nu' - \nu'') \right]$$

or we can simplify as,

$$\frac{\Delta \tilde{G}_{\nu'}}{(\nu' - \nu'')} = \tilde{\nu}_0 - \tilde{\nu}_0 x_e [\nu' + \nu'' + 1] = (\tilde{\nu}_0 - \tilde{\nu}_0 x_e) - \tilde{\nu}_0 x_e (\nu' + \nu'')$$

Therefore a plot of the left-hand side as a function of  $(\nu' + \nu'')$  will yield a straight line, from which  $\tilde{\nu}_0$  and  $x_e$  can be calculated. If we consider the case where  $\nu' - \nu'' = 1$ , the left hand side is simply the observed fundamental and overtone signals, and the analysis is particularly simple.

b. From the data given above, we obtain the following plot.

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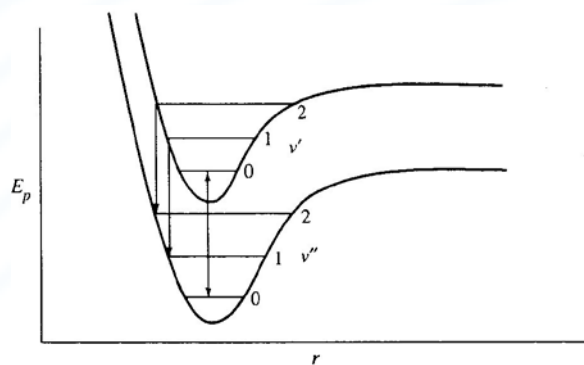
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**13.43.** Sketch potential energy curves for a diatomic molecule in its ground electronic state and in an excited state, consistent with the following observations:

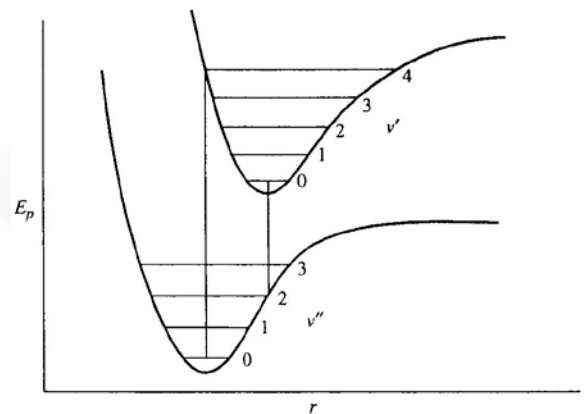
- There is a strong  $0 \leftarrow 0$  absorption band, and strong  $0 \rightarrow 0$ ,  $1 \rightarrow 1$ , and  $2 \rightarrow 2$  emission bands.
- The strongest absorption band is  $4 \leftarrow 0$ , and the strongest emission band is  $0 \rightarrow 2$ .
- There is no sharp rotational fine structure in absorption, but there is a sharp emission spectrum.
- The absorption spectrum shows a well-defined fine structure for the  $0 \leftarrow 0$ ,  $1 \leftarrow 0$ ,  $2 \leftarrow 0$ ,  $3 \leftarrow 0$ , and  $4 \leftarrow 0$  transitions and for the  $6 \leftarrow 0$  and  $7 \leftarrow 0$ , but not in between.

**Solution:**

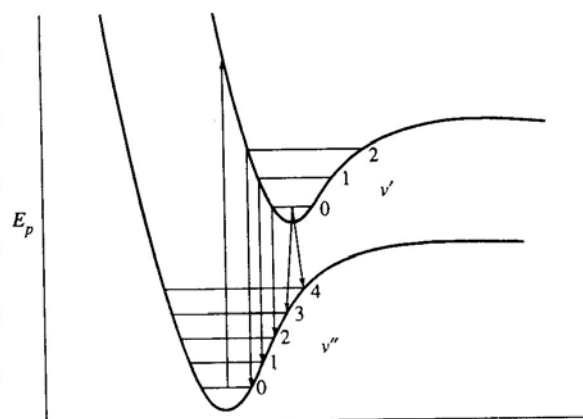
a.



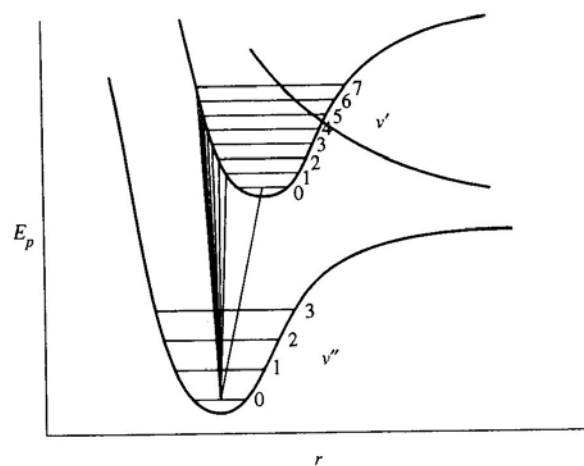
b.



c.



d.

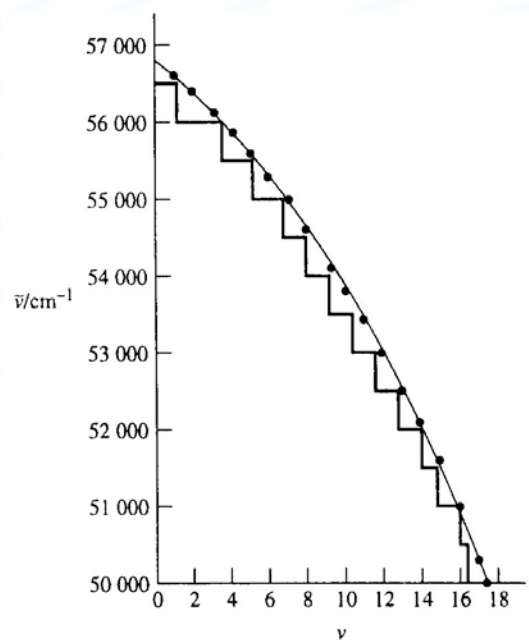
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**\*13.44.** Using the data in Example 13.12 on p. 702, determine the area under the curve in a plot of  $\Delta\nu$  against  $\nu$ . Extrapolate to zero  $\Delta\nu$  to obtain  $\nu'_{\max}$ , since the Birge-Sponer extrapolation shows that at that point  $\nu' = \nu'_{\max}$ . A better value may be obtained by a nonlinear extrapolation. What are the values of  $\nu'$  not given in the table?

**Solution:**

Given: Example 13.12

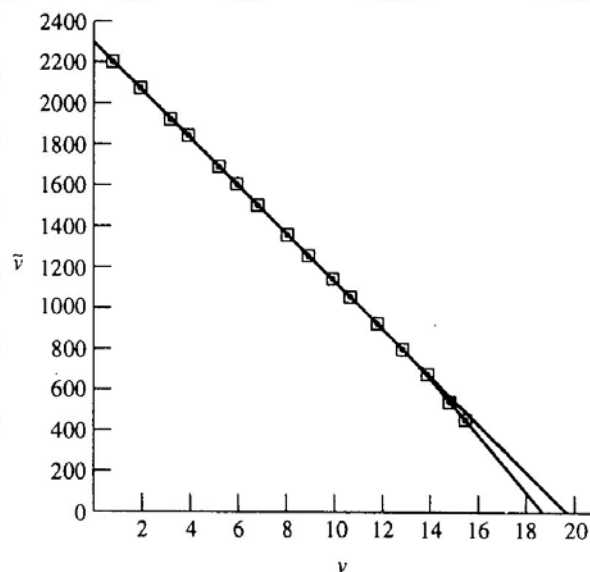
Required: area under the curve, values of  $\nu'$  not given in the table



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- 13.45.** Calculate the dissociation energy of the hydrogen molecule ion from the vibrational energy level separations of  $\text{H}_2^+$ . The values for the transitions  $1 \leftarrow 0, 2 \leftarrow 1, \dots$ , are, respectively, 2191, 2064, 1941, 1821, 1705, 1591, 1479, 1368, 1257, 1145, 1033, 918, 800, 677, 548, 411, with all values given in  $\text{cm}^{-1}$ . Use both a linear plot and a curve to obtain answers.



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**13.46.** The electronic spectra of diatomic molecules in the gas phase typically show extensive vibrational structure superimposed on the broader electronic transition. Taking the equilibrium geometry of the ground electronic state to be the zero energy, the  $\tilde{G}(\nu'')$  of Eq. 13.138 can be used to express the energies of the vibrational states  $\nu''$  (in  $\text{cm}^{-1}$ ) of this electronic state. Denoting the minimum energy of the excited electronic state as  $\tilde{T}_e$  (in  $\text{cm}^{-1}$ ), the vibrational energy levels  $\nu'$  of the excited state can be expressed as  $\tilde{T}_e + \tilde{G}(\nu')$ . Derive an expression for the frequencies  $\tilde{\nu}$  of the transitions  $\nu'' \rightarrow \nu'$  between the vibrational levels of the ground and excited electronic states. (Note that the vibrational frequencies and anharmonicity constants are not the same for the ground and excited electronic states.)

**Solution:**

Given: Eq. 13.138

Required: expression for  $\tilde{\nu}$

Eq. 13.138 is given by

$$G(\nu) = \tilde{\nu}_0 \left[ \left( \nu + \frac{1}{2} \right) - x_e \left( \nu + \frac{1}{2} \right)^2 \right]$$

The ground state vibrational energies are given by,

$$\tilde{G}_{\nu''} = \left( \nu'' + \frac{1}{2} \right) \tilde{\nu}_0'' - \left( \nu'' + \frac{1}{2} \right)^2 \tilde{\nu}_0'' x_e$$

And the excited state energies are expressed as,

$$\tilde{G}_{\nu'} = \tilde{T}_e + \left( \nu' + \frac{1}{2} \right) \tilde{\nu}_0' - \left( \nu' + \frac{1}{2} \right)^2 \tilde{\nu}_0' x_e$$

Therefore, the energy difference for the  $\nu'' \rightarrow \nu'$  transitions are given by,

$$\tilde{\nu} = \tilde{G}_{\nu'} - \tilde{G}_{\nu''} = \tilde{T}_e + \left[ \left( \nu' + \frac{1}{2} \right) \tilde{\nu}_0' - \left( \nu' + \frac{1}{2} \right)^2 \tilde{\nu}_0' x_e \right] - \left[ \left( \nu'' + \frac{1}{2} \right) \tilde{\nu}_0'' - \left( \nu'' + \frac{1}{2} \right)^2 \tilde{\nu}_0'' x_e \right]$$



This cannot be simplified any further.

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**13.47.** An easy and reliable way to analyze the electronic spectrum of a diatomic molecule is to use the equation derived in Problem 13.46 as the model for a multiple regression analysis (several plotting packages and mathematics packages such as Mathcad can perform this task) to simultaneously identify the five unknowns,  $\tilde{T}_e$ ,  $\tilde{\nu}'_0$ ,  $\tilde{\nu}'_0 x'_e$ ,  $\tilde{\nu}''_0$ , and  $\tilde{\nu}''_0 x''_e$  [McNaught, *J. Chem. Ed.* 57, 101(1980)]. The following data are from the electronic spectrum of iodine.

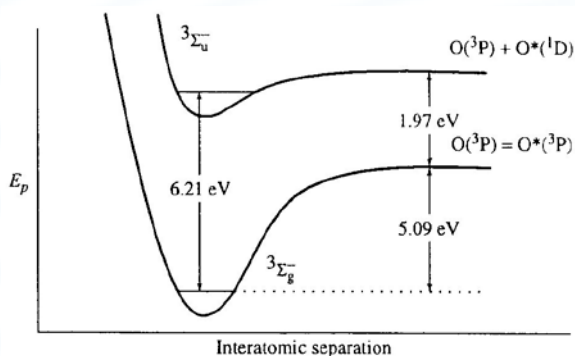
$0 \rightarrow v'$	$\lambda$ (nm)	$1 \rightarrow v'$	$\lambda$ (nm)	$2 \rightarrow v'$	$\lambda$ (nm)
17	567.2	15	581.0	10	607.3
18	564.2	16	577.8	11	603.1
19	561.5	17	574.2	12	599.1
20	558.5	18	571.3	13	595.5
21	555.8	19	568.3	14	591.8
22	553.0	20	565.2	15	588.1
23	550.1	21	559.6	16	584.8
24	547.8	22	556.9	17	581.2
25	542.7	23	554.2	18	578.1
26	540.7	24	551.8	19	575.1
27	538.5	25	549.0	20	572.4

Perform a multiple regression analysis and identify the spectroscopic parameters of the ground and excited electronic states. Literature values are (in  $\text{cm}^{-1}$ )  $\tilde{T}_e = 15730$ ,  $\tilde{\nu}'_0 = 132.1$ ,  $\tilde{\nu}'_0 x'_e = 1.051$ ,  $\tilde{\nu}''_0 = 214.5$ , and  $\tilde{\nu}''_0 x''_e = 0.614$ .

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**13.48.** The dissociation energy (from the zero-point level) of the ground state  $O_2(^3\Sigma_g^-)$  molecule is 5.09 eV. There exists an electronically excited  $^3\Sigma_u^-$  state of  $O_2$ , whose zero-point level lies 6.21 eV above the zero-point level of the ground state. The ground-state molecule dissociates into two ground-state  $O(^3P)$  atoms, while the  $^3\Sigma_u^-$  species dissociates into one ground-state  $O(^3P)$  atom and an  $O^*(^1D)$  atom that lies 1.97 eV above the ground state. Sketch the potential-energy curves and calculate the dissociation energy of  $O_2(^3\Sigma_u^-)$  into  $O + O^*(^1D)$ .



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**13.49.** The spectroscopic dissociation energy  $D_0$  is the energy required to dissociate the molecule in its ground vibrational state. This is always slightly smaller than the actual depth of the electronic potential energy because of the zero-point energy of the molecule (see Figure 13.22). Given that for HCl,  $D_e = 4.6173$  eV,  $\tilde{\nu}_0 = 2989$   $\text{cm}^{-1}$ , and  $\tilde{\nu}_0 x_e = 52.82$   $\text{cm}^{-1}$ , calculate the value of  $D_0$  for HCl.

**Solution:**

Given: HCl;  $D_e = 4.6173$  eV,  $\tilde{\nu}_0 = 2989$   $\text{cm}^{-1}$ ,  $\tilde{\nu}_0 x_e = 52.82$   $\text{cm}^{-1}$

Required:  $D_0$

To find the spectroscopic dissociation energy, we first calculate  $\tilde{G}_0$  from Eq. 13.138

$$G(\nu) = \tilde{\nu}_0 \left[ \left( \nu + \frac{1}{2} \right) - x_e \left( \nu + \frac{1}{2} \right)^2 \right]$$

$$\tilde{G}_0 = \tilde{\nu}_0 \left[ \left( 0 + \frac{1}{2} \right) - x_e \left( 0 + \frac{1}{2} \right)^2 \right]$$

$$\tilde{G}_0 = \frac{1}{2} \tilde{\nu}_0 - \frac{1}{4} \tilde{\nu}_0 x_e$$

$$\tilde{G}_0 = \frac{1}{2} \times 2989 \text{ cm}^{-1} - \frac{1}{4} \times 52.82 \text{ cm}^{-1}$$

$$\tilde{G}_0 = 1481.295 \text{ cm}^{-1}$$

$$\tilde{G}_0 = \frac{1481.295 \cancel{\text{cm}^{-1}} \times 2.998 \times 10^{10} \cancel{\text{cm}} \cancel{\text{s}^{-1}} \times 6.626 \times 10^{-34} \cancel{\text{J}} \cancel{\text{s}}}{1.602 \times 10^{-19} \cancel{\text{J}} (\text{eV})^{-1}}$$

$$\tilde{G}_0 = 0.1836801 \text{ eV}$$

To solve for  $D_0$ , we solve as follows,

$$D_0 = D_e - \left( \frac{1}{2} \tilde{\nu}_0 - \frac{1}{4} \tilde{\nu}_0 x_e \right)$$

$$\tilde{G}_0 = \frac{1}{2} \tilde{\nu}_0 - \frac{1}{4} \tilde{\nu}_0 x_e = 0.183\,680\,1\,\text{eV}$$

$$D_0 = 4.617\,3\,\text{eV} - 0.183\,680\,1\,\text{eV}$$

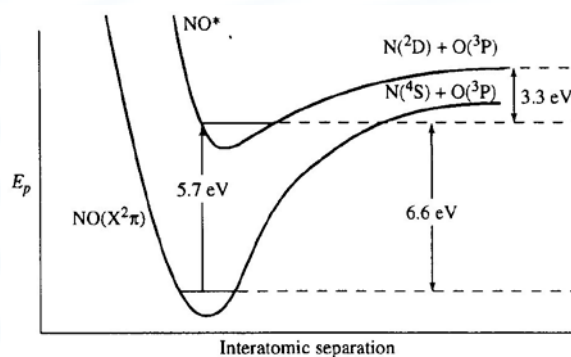
$$D_0 = 4.433\,619\,9\,\text{eV}$$

$$\boxed{D_0 = 4.433\,6\,\text{eV}}$$

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- 13.50.** The dissociation energy (from the zero-point level) of the ground state  $\text{NO}(X^2\pi)$  molecule is 6.6 eV. There exists an electronically excited  $\text{B}^2\Pi$  state of NO whose zero-point level lies at 5.7 eV above the zero-point level of the ground state. The ground-state molecule dissociates into ground state  $\text{N}(^4\text{S}) + \text{O}(^3\text{P})$ , while the  $\text{B}^2\Pi$  species dissociates into two ground-state atoms  $\text{N}(^2\text{D}) + \text{O}(^3\text{P})$  that lie 3.3 eV above its ground state. Sketch the potential energy curves and calculate the dissociation energy of NO into  $\text{N}(^2\text{D}) + \text{O}(^3\text{P})$ .

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**13.51.** Sodium vapor, which consists mainly of  $\text{Na}_2$  molecules, has a system of absorption bands in the green, the origin of the 0, 0 band being at  $20\,302.6\text{ cm}^{-1}$ . From the spacing of the vibrational levels it can be deduced that the dissociation energy of the upper state is 0.35 eV. The dissociation of the excited  $\text{Na}_2$  gives a normal atom and an atom that emits the yellow sodium D line at 589.3 nm. Calculate the energy of dissociation of  $\text{Na}_2$  in its ground state.

**Solution:**

Given:  $\text{Na}_2$ ;  $\tilde{\nu}_0 = 20\,302.6\text{ cm}^{-1}$ ,  $D_e = 0.35\text{ eV}$ ,  $\lambda = 589.3\text{ nm}$

Required:  $D_0$

The wavenumber  $20\,302.6\text{ cm}^{-1}$  corresponds to a frequency of,

$$\nu = 20\,302.6\text{ cm}^{-1} \times 2.998 \times 10^{10}\text{ cm s}^{-1}$$

$$\nu = 6.086\,72 \times 10^{14}\text{ s}^{-1}$$

And therefore an energy of,

$$E = h\nu$$

$$E = 6.626 \times 10^{-34}\text{ J s} \times 6.086\,72 \times 10^{14}\text{ s}^{-1}$$

$$E = 4.033\,06 \times 10^{-19}\text{ J}$$

$$E = \frac{4.033\,06 \times 10^{-19}\text{ J}}{1.602 \times 10^{-19}\text{ J (eV)}^{-1}}$$

$$E = 2.517\,515\,81\text{ eV}$$

The wavelength at 589.3 nm corresponds to a frequency of,

$$\nu = \frac{2.998 \times 10^8\text{ m s}^{-1}}{589.3\text{ m} \times 10^{-9}}$$

$$\nu = 5.087\,39 \times 10^{14}\text{ s}^{-1}$$

And therefore an energy of,

$$E = h\nu$$

$$E = 6.626 \times 10^{-34} \text{ J s} \times 5.08739 \times 10^{14} \text{ s}^{-1}$$

$$E = 3.37091 \times 10^{-19} \text{ J}$$

$$E = \frac{3.37091 \times 10^{-19} \text{ J}}{1.602 \times 10^{-19} \text{ J (eV)}^{-1}}$$

$$E = 2.104185905 \text{ eV}$$

The dissociation energy therefore becomes,

$$D_0 = 2.51751581 \text{ eV} + 0.35 \text{ eV} - 2.104185905 \text{ eV}$$

$$D_0 = 0.763329904 \text{ eV}$$

$$D_0 = 0.763329904 \text{ eV} \times 1.602 \times 10^{-19} \text{ J (eV)}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$D_0 = 73640.29841 \text{ J mol}^{-1}$$

$$D_0 = 73.6 \text{ kJ mol}^{-1}$$

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CHAPTER

# 14

Some Modern Applications  
of Spectroscopy

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LAIDLER . MEISER . SANCTUARY

Physical Chemistry

Electronic Edition

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Problems and Solutions

## Chapter 14

### Spectral Line Widths

- 14.1.** The sun emits a spectral line at 677.4 nm and it has been identified as due to an ionized  $^{57}\text{Fe}$  atom, which has a molar mass of 56.94 g mol $^{-1}$ . The spectral line has a width of 0.053 nm. Estimate the temperature of the surface of the sun.

[Solution](#)

- 14.2.** Estimate the lifetime of a state that, because of lifetime broadening, gives rise to a line of width
- 0.01 cm $^{-1}$ ,
  - 0.1 cm $^{-1}$ ,
  - 1.0 cm $^{-1}$ ,
  - 200 MHz.

[Solution](#)

- 14.3.** Lasers are commonly used in physical chemistry research laboratories to generate the reactive intermediates required in the study of elementary reactions. For example, highly reactive oxygen atoms in the ground electronic state [ $\text{O}(^3\text{P})$ ] can be generated from  $\text{NO}_2$  by laser-induced dissociation:  $\text{NO}_2 \xrightarrow{h\nu} \text{NO}(v', J') + \text{O}(^3\text{P})$ . The velocity distribution of the oxygen atoms thus generated (using a laser with  $\lambda = 355$  nm) shows two broad peaks centered at 900.00 and 1400.00 m s $^{-1}$ , respectively, and leads to the formation of the  $\text{NO}(v' = 0)$  and the  $\text{NO}(v' = 1)$  states [Hradil et al., *J. Chem. Phys.* 99, 4455(1993)].
- Identify the NO vibrational state that corresponds to each O atom velocity peak, and justify your choice.
  - If a total of 7400 cm $^{-1}$  of energy is available to the fragments, what are the velocities of the NO fragment corresponding to each of the peaks in the oxygen velocity distribution? (These velocities are measured with respect to a fixed laboratory coordinate system and, therefore, are the “absolute” velocities of the fragments. Assume that the NO molecules are the  $J = 0$  rotational state.) For the NO molecule,  $\tilde{\nu}_0 = 1904$  cm $^{-1}$ .

[Solution](#)

### Resonance Spectroscopy

- 14.4.** Calculate the magnetic flux density that is required to bring a free electron ( $g = 2.0023$ ) into resonance in an EPR spectrometer operating at a wavelength of 8.00 mm.

[Solution](#)

- 14.5.** An EPR spectrometer is operated at a frequency of 10.42 GHz and a study is made of methyl radicals. Resonance is observed at a magnetic flux density of 0.37175 T.
- Calculate the  $g$  value of the methyl radical.
  - Calculate the field required for resonance when the spectrometer is operating at 9.488 GHz.

[Solution](#)

- 14.6.** How many hyperfine lines would you expect to find in the ESR spectrum of  $^2\text{H}$ ,  $^{19}\text{F}$ ,  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$ ? Calculate the nuclear magnetic moment in each case. (Refer to Table 14.1, p. 735.)

[Solution](#)

- 14.7.** Determine the number of hyperfine lines expected in the ESR spectrum of  $^{63}\text{Cu}$ , which has a spin  $I$  of 1.

[Solution](#)

- 14.8.** In a nuclear magnetic resonance instrument operating at a frequency of 60 MHz, at what magnetic fields would you expect to observe resonance with  $^1\text{H}^{35}\text{Cl}$ ?

[Solution](#)

- 14.9.** The chemical shift  $\delta$  of methyl protons in acetaldehyde is 2.20 ppm, and that of the aldehydic proton is 9.80 ppm. What is the difference in the effective magnetic field for the two types of proton when the applied field is 1.5 T? If resonance is observed at 60 MHz, what is the splitting between the methyl and aldehyde proton resonances?

[Solution](#)

- 14.10** The nuclear spin quantum number  $I$  of the  $^{39}\text{K}$  nucleus is  $\frac{3}{2}$ , and the nuclear  $g$  factor is 0.2606. How many orientations does the nucleus have in a magnetic field? At what frequency would there be resonance in a field of 1.0 T?

[Solution](#)

- 14.11.** The  $^{11}\text{B}$  nucleus has a spin  $I$  of  $\frac{3}{2}$  and a nuclear  $g$  factor of 1.7920. At what field would resonance be observed at 60 MHz?

[Solution](#)

- 14.12.** The Fourier transform is the mathematical foundation for much of modern spectroscopy. The idea behind Fourier transform spectroscopy is to use a pulse of energy, which contains many frequencies, to probe the sample many times each second. The cumulative signal recorded from the pulses, which is a time-dependent oscillatory function  $F(t)$ , has the general form shown in Figure 14.25a. The Fourier transform of such a function results in a function of frequencies, which we may denote  $I(\omega)$ , obtained as

$$I(\omega) = A \operatorname{Re} \left[ \int_0^\infty F(t) e^{i\omega t} dt \right]$$

where Re represents the real part of the function. Perform the Fourier transform of  $F(t) = [\cos(\omega_1 t) + \cos(\omega_2 t)] \exp(-t/T)$ , where  $T$  is a relaxation time, and obtain an expression for  $I(\omega)$ . Analyze the behavior of this function by assigning arbitrary values to the constants and plotting it as a function of  $\omega$ . Use the fact that  $e^{i\omega t} = \cos \omega t + i \sin \omega t$ , and

$$\int_0^\infty \cos(at) \cos(bt) e^{-t/T} dt = T \frac{[1 + (a^2 + b^2)T^2]}{[1 + (a - b)^2 T^2][1 + (a + b)^2 T^2]}$$

[Solution](#)

- 14.13.** The lifetime of  $^{57}\text{Fe}^*$  is  $2 \times 10^{-7}$  s. Calculate the uncertainty in the frequency of the  $\gamma$  radiation emitted and in the wavenumber.

[Solution](#)

- 14.14.** The free radical  $\text{CH}_3$  is found experimentally to be planar. Give an interpretation of this result in terms of orbital hybridization. What microwave spectrum would the radical show? What vibrations would be active in the infrared?

[Solution](#)

- 14.15.** A complete photoelectron spectrum of the nitrogen molecule (see Figure 14.45) is given by Bock and Mollère [*J. Chem. Educ.* 51, 506(1974)]. The spectrum extends from about 411 eV (the peak corresponding to the  $1s\sigma_g$  is at approximately 410 eV) to about 15.0 eV, with the peak corresponding to the  $2p\sigma_g$  electron occurring at 15.88 eV. If we were to use a radiation source of wavelength 58.4 nm, which of the peaks in the spectrum can be studied? What will be the wavelength required to extend the range to 410 eV?

[Solution](#)

For additional problems, see the books listed at the end of the problem section in Chapter 12 (p. 634).

### Essay Questions

- 14.16.** Explain the selection rules for Raman spectra, with examples.  
**14.17.** Describe the physical interaction that leads to nuclear magnetic resonance.  
**14.18.** Give an account of the fundamental principles underlying Mössbauer spectroscopy.

**Solutions**

**14.1.** The sun emits a spectral line at 677.4 nm and it has been identified as due to an ionized  $^{57}\text{Fe}$  atom, which has a molar mass of 56.94 g mol $^{-1}$ . The spectral line has a width of 0.053 nm. Estimate the temperature of the surface of the sun.

**Solution:**

Given:  $^{57}\text{Fe}$ ,  $\lambda = 677.4 \text{ nm}$ ,  $M = 56.94 \text{ g mol}^{-1}$ ,  $\Delta\lambda = 0.053 \text{ nm}$

Required:  $T$

To solve this problem we need to use Eq. 14.4.

$$\Delta\nu = 2\left(\frac{\nu}{c}\right)(2k_{\text{B}}T/m)^{1/2}$$

Through substitution and rearrangement, Eq. 14.4, gives an expression for temperature in terms of wavelength.

$$\Delta\lambda = 2\left(\frac{\lambda}{c}\right)(2k_{\text{B}}T/m)^{1/2}$$

$$T = \left(\frac{\Delta\lambda c}{2\lambda}\right)^2 \frac{m}{2k_{\text{B}}}$$

$$m = \frac{M}{L}$$

$$T = \left(\frac{0.053 \times 10^{-9} \cancel{\text{m}} \times 2.998 \times 10^8 \text{ m s}^{-1}}{2 \times 677.4 \times 10^{-9} \cancel{\text{m}}}\right)^2 \left(\frac{56.94 \cancel{\text{g}} \cancel{\text{mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{g}^{-1}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}}\right) \left(\frac{1}{2 \times 1.381 \times 10^{-23} \text{ J K}^{-1}}\right)$$

$$T = 470\,888.037\,5 \text{ m}^2 \text{ s}^{-2} \cancel{\text{kg}} \cancel{\text{J}^{-1}} \text{ K}$$

$$\boxed{T = 4.71 \times 10^5 \text{ K}}$$

Therefore the temperature of the sun is approximately  $4.71 \times 10^5 \text{ K}$ .

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**14.2.** Estimate the lifetime of a state that, because of lifetime broadening, gives rise to a line of width

- a.  $0.01 \text{ cm}^{-1}$ ,
- b.  $0.1 \text{ cm}^{-1}$ ,
- c.  $1.0 \text{ cm}^{-1}$ ,
- d. 200 MHz.

**Solution:**

Given:  $\Delta\tilde{\nu}$ ,  $\Delta\nu$

Required:  $\Delta\tau$

The lifetime of a state is given by  $\Delta\tau$  and can be determined by rearranging Eq. 14.3

$$\Delta\tilde{\nu}/\text{cm}^{-1} \approx \frac{2.7 \times 10^{-12}}{\Delta\tau/\text{s}}$$

$$\Delta\tau = \frac{2.7 \times 10^{-12}}{\Delta\tilde{\nu}/\text{cm}^{-1}} \text{ s}$$

a. 
$$\Delta\tau = \frac{2.7 \times 10^{-12}}{0.01} \text{ s}$$

$$\boxed{\Delta\tau = 2.7 \times 10^{-10} \text{ s}}$$

b. 
$$\Delta\tau = \frac{2.7 \times 10^{-12}}{0.1} \text{ s}$$

$$\boxed{\Delta\tau = 2.7 \times 10^{-11} \text{ s}}$$

c. 
$$\Delta\tau = \frac{2.7 \times 10^{-12}}{1.0} \text{ s}$$

$$\boxed{\Delta\tau = 2.7 \times 10^{-12} \text{ s}}$$

d. In this case, we first need to convert as follows,

$$\Delta\tau = \frac{2.7 \times 10^{-12} \times 2.998 \times 10^{10} \text{ cm s}^{-1}}{200 \times 10^6 \text{ s}^{-1}} \text{ s}$$

$$\Delta\tau = 4.0473 \times 10^{-10} \text{ s}$$

$$\boxed{\Delta\tau = 4.05 \times 10^{-10} \text{ s}}$$

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- 14.3.** Lasers are commonly used in physical chemistry research laboratories to generate the reactive intermediates required in the study of elementary reactions. For example, highly reactive oxygen atoms in the ground electronic state [ $O(^3P)$ ] can be generated from  $NO_2$  by laser-induced dissociation:  $NO_2 \xrightarrow{h\nu} NO(v', J') + O(^3P)$ . The velocity distribution of the oxygen atoms thus generated (using a laser with  $\lambda = 355$  nm) shows two broad peaks centered at  $900.00$  and  $1400.00$  m s<sup>-1</sup>, respectively, and leads to the formation of the  $NO(v' = 0)$  and the  $NO(v' = 1)$  states [Hradil et al., *J. Chem. Phys.* 99, 4455(1993)].
- Identify the NO vibrational state that corresponds to each O atom velocity peak, and justify your choice.
  - If a total of  $7400$  cm<sup>-1</sup> of energy is available to the fragments, what are the velocities of the NO fragment corresponding to each of the peaks in the oxygen velocity distribution? (These velocities are measured with respect to a fixed laboratory coordinate system and, therefore, are the “absolute” velocities of the fragments. Assume that the NO molecules are the  $J = 0$  rotational state.) For the NO molecule,  $\tilde{\nu}_0 = 1904$  cm<sup>-1</sup>.

**Solution:**

Given:  $\lambda = 355$  nm,  $u_1 = 900.00$ ,  $u_2 = 1400.00$  m s<sup>-1</sup>,  $\tilde{\nu}_{\text{tot}} = 7400$  cm<sup>-1</sup>,  $\tilde{\nu}_0 = 1904$  cm<sup>-1</sup>

Required: NO vibrational state,  $v'$ ,  $v''$

- In this experiment, the energy absorbed by the  $NO_2$  molecule is used for bond dissociation to produce  $NO(v' = 0, 1) + O(^3P)$ , and the remaining energy is given to the translational motion of the two fragments. Since it takes less energy to form the  $NO(v' = 0)$  than the  $NO(v' = 1)$  state, the formation of  $NO(v' = 0)$  will correspond to higher O atom velocity. (Actually, higher velocities of both fragments)
- To find the velocities of the NO fragments corresponding to each of the peaks in the oxygen velocity distribution, we first calculate the energy of the O atom fragment corresponding to each peak.

at  $u_1 = 900.00$  m s<sup>-1</sup>:

$$E_O = \frac{1}{2} m_O u_O^2$$

$$E_O = \frac{1}{2} \times \frac{0.016 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times (900.00 \text{ m s}^{-1})^2$$

$$E_O = 1.07605 \times 10^{-20} \text{ kg m}^2 \text{ s}^{-2}$$

$$E_O = 1.07605 \times 10^{-20} \text{ J}$$



at  $u_2 = 1\,400.00\text{ m s}^{-1}$  :

$$E_0 = \frac{1}{2} \times \frac{0.016\text{ kg} \cancel{\text{mol}^{-1}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}} \times (1\,400.00\text{ m s}^{-1})^2$$

$$E_0 = 2.603\,79 \times 10^{-20}\text{ J}$$

The energy of the NO molecule in the

$v' = 0$  state:

$$E_0 = \frac{1}{2} hc\tilde{\nu}_0$$

$$E_0 = \frac{1}{2} \times 6.626 \times 10^{-34}\text{ J} \cancel{s} \times 2.998 \times 10^{10} \cancel{\text{cm}} \cancel{s^{-1}} \times 1\,904 \cancel{\text{cm}^{-1}}$$

$$E_0 = 1.891\,12 \times 10^{-20}\text{ J}$$

$v' = 1$  state:

$$E_1 = \frac{3}{2} hc\tilde{\nu}_0$$

$$E_1 = \frac{3}{2} \times 6.626 \times 10^{-34}\text{ J} \cancel{s} \times 2.998 \times 10^{10} \cancel{\text{cm}} \cancel{s^{-1}} \times 1\,904 \cancel{\text{cm}^{-1}}$$

$$E_1 = 5.673\,37 \times 10^{-20}\text{ J}$$

$$E_{\text{tot}} = hc\tilde{\nu}_{\text{tot}}$$

Since the total energy available to the fragments is  $E_{\text{tot}} = 6.626 \times 10^{-34}\text{ J} \cancel{s} \times 2.998 \times 10^{10} \cancel{\text{cm}} \cancel{s^{-1}} \times 7\,400 \cancel{\text{cm}^{-1}}$

$$E_{\text{tot}} = 1.469\,99 \times 10^{-19}\text{ J}$$

The translational energy available to the NO fragment (since rotational energy is zero) will be,

$$E_{\text{tr}}(\text{NO}) = E_{\text{tot}} - \left( E_{v'} + \frac{1}{2} m_{\text{O}} u_{\text{O}}^2 \right)$$

$$\text{and therefore } u_{\text{NO}} = \sqrt{\frac{E_{\text{tr}}(\text{NO})}{m_{\text{NO}}}}$$

$$\text{at } v' = 1, u_{\text{O}} = 900.00 \text{ m s}^{-1} :$$

$$E_{\text{tr}}(\text{NO}) = 1.469\,99 \times 10^{-19} \text{ J} - (5.673\,37 \times 10^{-20} \text{ J} + 1.076\,05 \times 10^{-20} \text{ J})$$

$$E_{\text{tr}}(\text{NO}) = 7.950\,49 \times 10^{-20} \text{ J}$$

$$u_{\text{NO}} = \sqrt{\frac{E_{\text{tr}}(\text{NO})}{m_{\text{NO}}}}$$

$$u_{\text{NO}} = \sqrt{\frac{7.950\,49 \times 10^{-20} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{0.03 \text{ kg mol}^{-1}}}$$

$$u_{\text{NO}} = 1\,263.300\,345 \text{ m s}^{-1}$$

$$\boxed{u_{\text{NO}} = 1\,263 \text{ m s}^{-1}}$$

$$\text{at } v' = 0, u_{\text{O}} = 1\,400.00 \text{ m s}^{-1} :$$

$$E_{\text{tr}}(\text{NO}) = 1.469\,99 \times 10^{-19} \text{ J} - (1.891\,12 \times 10^{-20} \text{ J} + 2.603\,79 \times 10^{-20} \text{ J})$$

$$E_{\text{tr}}(\text{NO}) = 1.020\,5 \times 10^{-19} \text{ J}$$

$$u_{\text{NO}} = \sqrt{\frac{1.020\,5 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{0.03 \text{ kg mol}^{-1}}}$$

$$u_{\text{NO}} = 1\,431.252\,72 \text{ m s}^{-1}$$

$$\boxed{u_{\text{NO}} = 1\,431 \text{ m s}^{-1}}$$

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**14.4.** Calculate the magnetic flux density that is required to bring a free electron ( $g = 2.0023$ ) into resonance in an EPR spectrometer operating at a wavelength of 8.00 mm.

**Solution:**

Given:  $g = 2.0023$ ,  $\lambda = 8.00$  mm

Required:  $B$

To calculate the magnetic flux density, we can use Eq. 14.43,

$$\Delta E = h\nu = g\mu_B B_0$$

Rearranging, we obtain

$$B = \frac{h\nu}{g\mu_B}$$

Converting the wavelength to frequency, and then solving, we obtain  $B$  as,

$$\nu = \frac{c}{\lambda}$$

$$B = \frac{h}{g\mu_B} \frac{c}{\lambda}$$

$$B = \frac{6.626 \times 10^{-34} \cancel{\text{J}} \cancel{\text{s}}}{2.023 \times 9.274 \times 10^{-24} \cancel{\text{J}} \text{T}^{-1}} \frac{2.998 \times 10^8 \cancel{\text{m}} \cancel{\text{s}^{-1}}}{8.00 \times 10^{-3} \cancel{\text{m}}}$$

$$B = 1.323\,518\,752 \text{ T}$$

$$\boxed{B = 1.32 \text{ T}}$$

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- 14.5.** An EPR spectrometer is operated at a frequency of 10.42 GHz and a study is made of methyl radicals. Resonance is observed at a magnetic flux density of 0.37175 T.
- Calculate the  $g$  value of the methyl radical.
  - Calculate the field required for resonance when the spectrometer is operating at 9.488 GHz.

**Solution:**

Given:  $\nu = 10.42$  GHz,  $B = 0.37175$  T

Required:  $g$ ,  $B$  at  $\nu = 9.488$  GHz

- a. To solve for the  $g$  value of the methyl radical, we use Eq. 14.43,

$$\Delta E = h\nu = g\mu_B B_o$$

Rearranging, we obtain

$$g = \frac{h\nu}{B\mu_B}$$

$$g = \frac{6.626 \times 10^{-34} \cancel{\text{J}} \cancel{\text{s}} \times 10.42 \times 10^9 \cancel{\text{s}^{-1}}}{0.37175 \cancel{\text{T}} \times 9.274 \times 10^{-24} \cancel{\text{J}} \cancel{\text{T}^{-1}}}$$

$$g = 2.002631679$$

$$\boxed{g = 2.003}$$

- b. To calculate the magnetic field at  $\nu = 9.488$  GHz, we can use Eq. 14.43 in the form of,

$$B = \frac{h\nu}{g\mu_B}$$

$$B = \frac{6.626 \times 10^{-34} \cancel{\text{J}} \cancel{\text{s}} \times 9.488 \times 10^9 \cancel{\text{s}^{-1}}}{2.002631679 \cancel{\text{T}} \times 9.274 \times 10^{-24} \cancel{\text{J}} \cancel{\text{T}^{-1}}}$$

$$B = 0.338499424 \text{ T}$$

$$\boxed{B = 0.3385 \text{ T}}$$

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**14.6.** How many hyperfine lines would you expect to find in the ESR spectrum of  $^2\text{H}$ ,  $^{19}\text{F}$ ,  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$ ? Calculate the nuclear magnetic moment in each case. (Refer to Table 14.1, p. 735.)

**Solution:**

Given:  $^2\text{H}$ ,  $^{19}\text{F}$ ,  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$

Required: hyperfine lines,  $\mu_N$  for each

	$^2\text{H}$	$^{19}\text{F}$	$^{35}\text{Cl}$	$^{37}\text{Cl}$
Spin, $I$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
$M_I$ values	1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$+\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$
Number of lines	3	2	4	4
$g_N$ (from Table 14.1)	0.857387	5.257	0.54727	0.4555
$\mu_N / 10^{-27} \text{ J T}^{-1}$				

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**14.7.** Determine the number of hyperfine lines expected in the ESR spectrum of  $^{63}\text{Cu}$ , which has a spin  $I$  of 1.

**Solution:**

Given:  $^{63}\text{Cu}$ ,  $I = 1$ .

Required: number of hyperfine lines

The number of hyperfine lines corresponds to the total number of  $M_I$  values. For  $I = 1$ ,  $M_I = 1, 0, -1$  and therefore three lines are expected.

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**14.8.** In a nuclear magnetic resonance instrument operating at a frequency of 60 MHz, at what magnetic fields would you expect to observe resonance with  $^1\text{H}^{35}\text{Cl}$ ?

**Solution:**

Given:  $\nu = 60 \text{ MHz}$

Required:  $B$  at which the instrument resonates with  $^1\text{H}^{35}\text{Cl}$

To calculate  $B$ , we use Eq. 14.43 to first determine the energy which corresponds to  $\nu = 60 \text{ MHz}$ .

$$\Delta E = h\nu = g\mu_B B_0$$

$$\Delta E = 6.626 \times 10^{-34} \text{ J s} \times 60 \times 10^6 \text{ s}^{-1}$$

$$\Delta E = 3.9756 \times 10^{-26} \text{ J}$$

Resonance could be observed with the proton and with  $^{35}\text{Cl}$ .

For the proton we use the  $g_N$  value for  $^1\text{H}$  in Table 14.1,

$$\Delta E = g_N \mu_N B$$

$$B = \frac{\Delta E}{g_N \mu_N}$$

$$B = \frac{3.9756 \times 10^{-26} \text{ J}}{5.5856 \times 5.0508 \times 10^{-27} \text{ J T}^{-1}}$$

$$B = 1.409200143 \text{ T}$$

$$\boxed{B = 1.41 \text{ T}}$$

For  $^{35}\text{Cl}$ , we use the  $g_N$  value found in Table 14.1,

$$\Delta E = g_N \mu_N B$$

$$B = \frac{\Delta E}{g_N \mu_N}$$

$$B = \frac{3.9756 \times 10^{-26} \text{ J}}{0.54727 \times 5.0508 \times 10^{-27} \text{ J T}^{-1}}$$

$$B = 14.38271478 \text{ T}$$

$$\boxed{B = 14.4 \text{ T}}$$

(This is outside the normal instrumental range).

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**14.9.** The chemical shift  $\delta$  of methyl protons in acetaldehyde is 2.20 ppm, and that of the aldehydic proton is 9.80 ppm. What is the difference in the effective magnetic field for the two types of proton when the applied field is 1.5 T? If resonance is observed at 60 MHz, what is the splitting between the methyl and aldehyde proton resonances?

**Solution:**

Given:  $\delta_{\text{Methyl}} = 2.20$  ppm,  $\delta_{\text{Aldehydic}} = 9.80$  ppm,  $B = 1.5$  T,  $\nu = 60$  MHz

Required:  $\Delta B_{\text{eff}}$ ,  $\nu$

The effective magnetic field is given by,

$$\Delta B_{\text{eff}} = -\Delta\sigma B$$

$$\Delta B_{\text{eff}} = -(9.80 - 2.20) \times 10^{-6} \times 1.5 \text{ T}$$

$$\Delta B_{\text{eff}} = -1.14 \times 10^{-5}$$

$$\boxed{\Delta B_{\text{eff}} = -11.4 \mu\text{T}}$$

The frequency splitting can be calculated by multiplying the difference in shifts by 60 MHz,

$$\nu = \Delta\sigma \times 60 \times 10^6 \text{ s}^{-1}$$

$$\nu = (9.80 - 2.20) \times 10^{-6} \times 60 \times 10^6 \text{ s}^{-1}$$

$$\boxed{\nu = 456 \text{ Hz}}$$

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**14.10** The nuclear spin quantum number  $I$  of the  $^{39}\text{K}$  nucleus is  $\frac{3}{2}$ , and the nuclear  $g$  factor is 0.2606. How many orientations does the nucleus have in a magnetic field? At what frequency would there be resonance in a field of 1.0 T?

**Solution:**

Given:  $^{39}\text{K}$ ,  $I = \frac{3}{2}$ ,  $g_N = 0.2606$ ,  $B = 1.0\text{ T}$

Required: number of orientations,  $\nu$

The number of orientations of the nucleus in a magnetic field is the total number of  $M_I$  values,

$$M_I = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

Therefore there are four orientations in the magnetic field.

To calculate  $\nu$ , we rearrange Eq. 14.43 in the following manner,

$$\Delta E = h\nu = g_N \mu_N B$$

$$\nu = \frac{g_N \mu_N B}{h}$$

$$\nu = \frac{0.2606 \times 5.0508 \times 10^{-27} \cancel{\text{J}} \cancel{\text{T}} \times 1.0 \cancel{\text{T}}}{6.626 \times 10^{-34} \cancel{\text{J}} \text{ s}}$$

$$\nu = 1986475.219\text{ Hz}$$

$$\boxed{\nu = 1.986\text{ MHz}}$$

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**14.11.** The  $^{11}\text{B}$  nucleus has a spin  $I$  of  $\frac{3}{2}$  and a nuclear  $g$  factor of 1.7920. At what field would resonance be observed at 60 MHz?

**Solution:**

Given:  $^{11}\text{B}$ ,  $I = \frac{3}{2}$ ,  $g_N = 1.7920$ ,  $\nu = 60 \text{ MHz}$

Required:  $B$

To calculate  $B$ , we rearrange Eq. 14.43 in the following manner,

$$\Delta E = h\nu = g_N \mu_N B$$

$$B = \frac{h\nu}{g_N \mu_N}$$

$$B = \frac{6.626 \times 10^{-34} \cancel{\text{J}} \times 60 \times 10^6 \cancel{\text{s}^{-1}}}{1.7920 \times 5.0508 \times 10^{-27} \cancel{\text{J}} \text{ T}^{-1}}$$

$$B = 4.392426518 \text{ T}$$

$$\boxed{B = 4.3924 \text{ T}}$$

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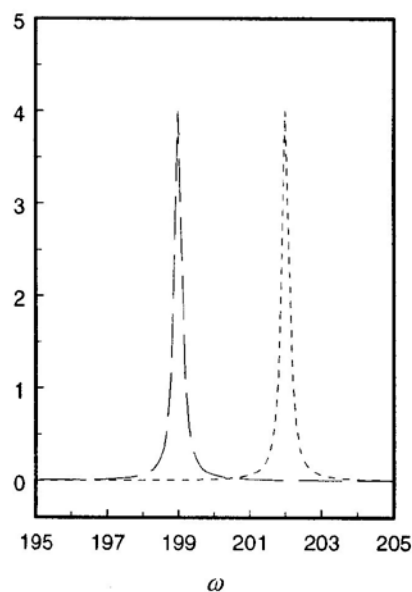
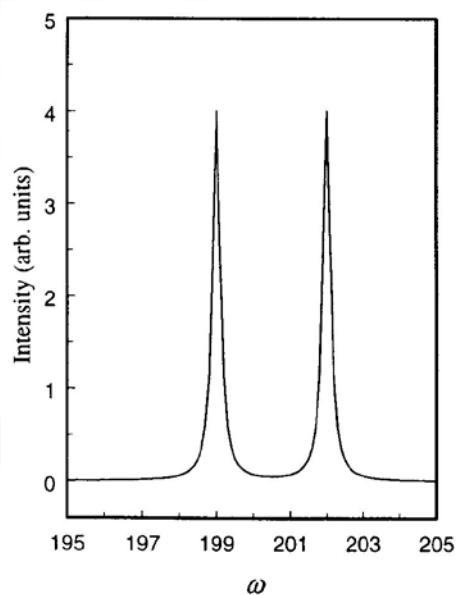
**14.12.** The Fourier transform is the mathematical foundation for much of modern spectroscopy. The idea behind Fourier transform spectroscopy is to use a pulse of energy, which contains many frequencies, to probe the sample many times each second. The cumulative signal recorded from the pulses, which is a time-dependent oscillatory function  $F(t)$ , has the general form shown in Figure 14.25a. The Fourier transform of such a function results in a function of frequencies, which we may denote  $I(\omega)$ , obtained as

$$I(\omega) = A \operatorname{Re} \left[ \int_0^\infty F(t) e^{i\omega t} dt \right]$$

where  $\operatorname{Re}$  represents the real part of the function. Perform the Fourier transform of  $F(t) = [\cos(\omega_1 t) + \cos(\omega_2 t)] \exp(-t/T)$ , where  $T$  is a relaxation time, and obtain an expression for  $I(\omega)$ . Analyze the behavior of this function by assigning arbitrary values to the constants and plotting it as a function of  $\omega$ . Use the fact that  $e^{i\omega t} = \cos \omega t + i \sin \omega t$ , and

$$\int_0^\infty \cos(at) \cos(bt) e^{-t/T} dt = T \frac{[1 + (a^2 + b^2)T^2]}{[1 + (a - b)^2 T^2][1 + (a + b)^2 T^2]}$$

**Solution:**



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**14.13.** The lifetime of  $^{57}\text{Fe}^*$  is  $2 \times 10^{-7}\text{s}$ . Calculate the uncertainty in the frequency of the  $\gamma$  radiation emitted and in the wavenumber.

**Solution:**

Given:  $^{57}\text{Fe}^*$ ,  $\Delta\tau = 2 \times 10^{-7}\text{s}$

Required: uncertainty in  $\Delta\nu$ ,  $\Delta\tilde{\nu}$

From the uncertainty principle we have Eq. 14.2,

$$\Delta E \Delta\tau \geq \hbar/2$$

And therefore an energy of,

$$\Delta E = \frac{h}{4\pi\Delta\tau}$$

$$\Delta E = \frac{6.626 \times 10^{-34} \text{ J } \cancel{\text{s}}}{4\pi \times 2 \times 10^{-7} \cancel{\text{s}}}$$

$$\Delta E = 2.6364 \times 10^{-28} \text{ J}$$

We can solve for the uncertainty in the frequency is therefore

$$\Delta E = h\Delta\nu$$

$$\Delta\nu = \frac{\Delta E}{h}$$

$$\Delta\nu = \frac{2.6364 \times 10^{-28} \cancel{\text{J}}}{6.626 \times 10^{-34} \cancel{\text{J}} \text{ s}}$$

$$\Delta\nu = 397\,887.357\,7 \text{ s}^{-1}$$

$$\boxed{\Delta\nu = 3.98 \times 10^5 \text{ s}^{-1}}$$

In terms of wavenumbers, this becomes,

$$\Delta \tilde{\nu} = \frac{\Delta \nu}{c}$$

$$\Delta \tilde{\nu} = \frac{397\,887.357\,7\,\text{s}^{-1}}{2.998 \times 10^{10}\,\text{cm s}^{-1}}$$

$$\Delta \tilde{\nu} = \frac{397\,887.357\,7\,\cancel{\text{s}^{-1}}}{2.998 \times 10^{10}\,\text{cm}\,\cancel{\text{s}^{-1}}}$$

$$\Delta \tilde{\nu} = 1.327\,18 \times 10^{-5}\,\text{cm}^{-1}$$

$$\boxed{\Delta \tilde{\nu} = 1.33 \times 10^{-5}\,\text{cm}^{-1}}$$

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**14.14.** The free radical  $\text{CH}_3$  is found experimentally to be planar. Give an interpretation of this result in terms of orbital hybridization. What microwave spectrum would the radical show? What vibrations would be active in the infrared?

**Solution:**

The planar form of  $\text{CH}_3\bullet$  must arise from  $\text{sp}^2$  hybridization. This leads to the  $D_{3h}$  point group. Since planar  $\text{CH}_3\bullet$  has no dipole moment, it shows no microwave spectrum.

The vibrations that would be active in the infrared are shown in Figure 13.25 for  $\text{BF}_3$ . As discussed in the text, all normal modes except the completely symmetric one ( $a_1'$ ), give an infrared spectrum. In other words, an infrared spectrum is given by  $a_1''$  and  $e'$  vibrations.

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**14.15.** A complete photoelectron spectrum of the nitrogen molecule (see Figure 14.45) is given by Bock and Mollère [*J. Chem. Educ.* 51, 506(1974)]. The spectrum extends from about 411 eV (the peak corresponding to the  $1s\sigma_g$  is at approximately 410 eV) to about 15.0 eV, with the peak corresponding to the  $2p\sigma_g$  electron occurring at 15.88 eV. If we were to use a radiation source of wavelength 58.4 nm, which of the peaks in the spectrum can be studied? What will be the wavelength required to extend the range to 410 eV?

**Solution:**

Given:  $\lambda = 58.4 \text{ nm}$

Required: which peaks would be studied,  $\lambda$  to extend range to 410 eV

To determine the peak which would be studied, we first calculate the energy of the radiation with  $\lambda = 58.4 \text{ nm}$ ,

$$E = h\nu = \frac{hc}{\lambda}$$

$$E = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{58.4 \times 10^{-9} \text{ m}}$$

$$E = 3.4015 \times 10^{-18} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-18} \text{ J}}$$

$$E = 21.232 \text{ eV}$$

Therefore, this source can be used to study peaks with energy below 21.2 eV, which corresponds to all peaks shown in Figure 14.45.

In order to study peaks up to an energy of 410 eV, the wavelength of radiation required would be,

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{410 \text{ eV}} \times \frac{1 \text{ eV}}{1.602 \times 10^{-18} \text{ J}}$$

$$\lambda = 3.024 \times 10^{-9} \text{ m}$$

$$\boxed{\lambda = 3.02 \text{ nm}}$$

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CHAPTER

# 15

Statistical Mechanics

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LAIDLER . MEISER . SANCTUARY

**Physical Chemistry**

Electronic Edition

Publisher: MCH Multimedia Inc.

**Problems and Solutions**

**Chapter 15****Permutations and Combinations:**

- 15.1.** Use Stirling's formula to calculate and approximate value for  $\ln(N!)$  and compare with the exact value for  $N=5, 10, 50, 100, 1,000$  and  $10,000!$

[Solution](#)

Work out the following examples:

- 15.2.** The number of possible arrangements of 4 objects (A B C D) among 4 positions (do not list them).

[Solution](#)

- 15.3.** The number of possible arrangements of 3 objects (A B C) among 4 positions. List them all.

[Solution](#)

- 15.4.** Use the binomial distribution to work out the binomial coefficients for  $(x_1 + x_2)^n$  for  $n=5$ . Arrange the numbers in Pascal's triangle. Work out the quantities  $\binom{4}{3}$ ,  $\binom{5}{3}$  and  $\binom{5}{2}$  to check your entries.

[Solution](#)

- 15.5.** Consider two sets of indistinguishable objects, {A A} and {B B B}. Work out and list the possible arrangements of these in 5 boxes, one object per box. Check your number against the formula.

$$P_r^n = \frac{n!}{\prod_c n_c!}$$

[Solution](#)

- 15.6.** Work out the number of ways that the three objects (A B C) can be placed in 5 boxes, no more than one object per box. List all the possibilities to confirm your number.

[Solution](#)

- 15.7.** Work out the number of ways that the three objects (A A A) can be placed in 5 boxes, no more than one object per box. List all the possibilities to confirm your number.

$$C_r^n = \frac{n!}{(n-r)! r!}$$

[Solution](#)

- 15.8.** Work out the number of ways that the two objects (A B) can be placed in 3 boxes with no restriction on the number of objects per box. List all the possibilities to confirm your number.

[Solution](#)

- 15.9.** Work out the number of ways that the two objects (A A) can be placed in 4 boxes without restriction on the number of objects per box. List all the possibilities to confirm your number.

[Solution](#)

- 15.10.** When we remove the condition of distinguishability from the  $n$  objects of Eq.(A.5), we divide by  $n!$  to obtain Eq.(A.6). By considering the simple case of 2 objects and 3 boxes, (same as problem 2g) show that it is improper similarly to divide Eq.(A.7) by  $n!$  to obtain the desired result for Eq.(A.8).

[Solution](#)

- 15.11.** A partially deuterated methane sample is analyzed and found to contain equal molar quantities of hydrogen and deuterium. On a random basis, calculate the percentage of species  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ ,  $\text{CHD}_3$ ,  $\text{CD}_4$ .

[Solution](#)

### Quantum statistics

- 15.12.** Show that  $\ln \left[ \frac{m!}{n!(m-n)!} \right]$  and  $\ln \left[ \frac{(m+n-1)!}{n!(m-1)!} \right]$  both approach  $\ln \left[ \frac{m^n}{n!} \right]$  as  $n$  becomes large, provided that  $m \gg n$ . (Use Stirling's formula and use the fact that  $m \gg n$ , and  $m \gg 1$ .)

[Solution](#)

**15.13.** Show that the maximum entropy,  $S$ , is obtained when all the probabilities,  $p_i$  are equal, where

$$S = -\sum_{i=1}^n p_i \ln p_i \quad \text{and} \quad \sum_{i=1}^n p_i = 1$$

(This shows us that complete lack of knowledge of which state the system is in results in the highest entropy. When all states are equally likely, we have no preferential state, and this means the most random or highest entropy.)

[Solution](#)

**15.14.** Prove that for an  $N$  particle quantum state, the wave function must be either odd or even under the permutation of any two of the  $N$  particles.

(This symmetry, of course, distinguishes bosons from fermions.)

[Solution](#)

**15.15.** A more accurate form of Stirling's approximation is

$$\ln N! = N \ln N - N + \ln \sqrt{2\pi N}$$

In the stopcock opening and closing example, recalculate the effect of  $\Delta S_{II \rightarrow III}$  using the above approximation and show that the entropy change is negligible compared to  $\Delta S_{I \rightarrow II}$ . Assume that the two volumes are equal, and consider what happens to this new entropy change  $\Delta S_{II \rightarrow III} < 0$  as the number of particles goes to infinity

(Although we observe no noticeable change when we physically close the stopcock in going from state II to III, there is a change due to our definition. This problem asks you to look into. The reason the change is negligible from our theory is because we are dealing with an enormous number of particles, and can use Stirling's approximation. However, if we had only a few particles, then the effect of closing the stopcock would lead to a difference between the two states, II and III, i.e. the "entropy" would show a decrease. This underscores the fact that we can not define entropy for a small number of particles because entropy is a statistical quantity.)

[Solution](#)

**15.16.** Using:  $\frac{N_1}{V_1} = \frac{N_2}{V_2}$  prove the relationship:

$$\ln \left[ \frac{(V_1/V_c)^{N_1} (V_2/V_c)^{N_2} (N_1 + N_2)!}{\left( (V_1/V_c)^{N_1} + (V_2/V_c)^{N_2} \right) (N_1)! (N_2)!} \right] = \ln \left[ \frac{(N_1)^{N_1} N_2^{N_2} (N_1 + N_2)!}{(N_1^{N_1} + N_2^{N_2}) (N_1)! (N_2)!} \right]$$

[Solution](#)

**15.17.** Without considering energy, calculate the statistical weights for 30 quanta distributed amongst 30 oscillators for the following distributions of the quanta:

$$N_0 = 0, N_1 = 30, N_{2 \rightarrow 29} = 0$$

$$N_0 = 1, N_1 = 28, N_2 = 1, N_{3 \rightarrow 29} = 0$$

$$N_0 = 10, N_1 = 10, N_2 = 10, N_{3 \rightarrow 29} = 0$$

(This is a problem of combinatorials, how many ways can 30 indistinguishable objects be distributed between 30 levels. For oscillators, we usually label the lowest state by a “0”, so we go up to the 29<sup>th</sup> level. In general, there is usually degeneracy (more than one state with the same energy) Here we are calculating the degeneracy for various possible energies. In case a) the energy is  $30\varepsilon_1$ , for b) the energy is  $\varepsilon_0 + 28\varepsilon_1 + 2\varepsilon_2$  and for c)  $10\varepsilon_0 + 10\varepsilon_1 + 10\varepsilon_2$ . The problem calculates the number of ways (the statistical weight) that indistinguishable quantum can be arranged to give that particular energy.)

[Solution](#)

**15.18.** Show that Eq.(15.148) satisfies FD and BE conditions of respectively no more that 1 particle, on the average, in a state, and any number of particles in a state. Let  $x = \exp \left[ (\varepsilon_\alpha - \mu') / k_B T \right]$

[Solution](#)

**Transformations of statistical and thermodynamic functions****15.19.** Starting from

$$S = k_B \ln \Omega(E, V, N)$$

obtain the equation:

$$PV = k_B T \ln \Xi(T, V, \mu)$$

where  $\Xi(T, V, \mu)$  is the grand partition function. Do NOT derive the ideal gas law (i.e. do not assume the particles do not interact).

(The grand partition function is one that is commonly used in chemical reactions.)

[Solution](#)**15.20.** Derive expressions for the energy  $U=E$ , the entropy  $S$  the pressure  $P$  and the Helmholtz energy  $A$ , and the Gibbs energy  $G$  in terms of the Canonical ensemble,  $Q$ .[Solution](#)**15.21.** Find the natural function for the isothermal-isobaric ensemble,  $\Delta(T, P, N)$ , i.e. for variables  $T, P$  and  $N$ .[Solution](#)**15.22.** Obtain an expression for  $C_P$  in terms of the partition function  $Q$  for the system.[Solution](#)**15.23.** Obtain an expression for the pressure  $P$  in terms of the molecular partition function  $q$ , for (a) distinguishable molecules and (b) indistinguishable molecules. Express the result in terms of the number of molecules  $N$  and also the amount of substance  $n$ .[Solution](#)**15.24.** The partition function for each degree of vibrational freedom is  $1 / \left[ 1 - \exp \left( \frac{-h\nu}{k_B T} \right) \right]$  (Eq.(15.173)). Obtain from this expression the limiting value of the vibrational contribution to  $C_V$  as  $T$  approaches infinity.[Solution](#)

**15.25.** Chemical reactions often lead to the formation of products whose energy distributions show significant deviations from the statistical distribution of Eq. 15.40. In a study of an elementary reaction with  $^{16}\text{O}^1\text{H}$  radical as one of the products [Zhang, van der Zande, Bronikowski, and Zare, *J. Chem. Phys.* 94, 2704(1994)], the following rotational distribution was observed for the  $\text{OH}(\nu = 0)$  state (normalized such that  $\sum n_J/N = 1$ ). Compare this to the statistical distribution expected from Eq.(15.84) at 298 K. The equilibrium bond distance of OH is 0.96966 Å.

$J$	7	8	9	10	11	12	13
$n_J/N$	0.0181	0.0232	0.0356	0.0475	0.0377	0.0762	0.1045
$J$	14	15	16	17	18	19	20
$n_J/N$	0.1266	0.1459	0.1466	0.1306	0.0907	0.0167	0.0000

[Solution](#)

### Partition functions

**15.26.** Suppose that an array of harmonic oscillators has common frequency of  $\nu = 10^{11} \text{ s}^{-1}$ . Calculate the ratio of the number of oscillators in the 10<sup>th</sup> quantum state ( $n=9$ ) to those in the ground state at 0 K, 300 K and 1000 K. The energy levels are given by  $\varepsilon_n = (n + \frac{1}{2})h\nu$ .

(This is a straight application of the Boltzmann distribution. Each energy level is non-degenerate.)

[Solution](#)

**15.27.** Calculate the average value of the energy per mole at the various temperatures for the oscillators in problem 17.

(This is best done by evaluating the partition function for harmonic oscillators and applying the general formula for  $\langle \varepsilon \rangle$ .)

[Solution](#)



**15.28.** The energy levels for a harmonic oscillator are given by  $\varepsilon_n = \left( n + \frac{1}{2} \right) h\nu$ .

a. Derive an expression for the mean-square fluctuation,  $\sigma_E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2}$  in energy for these oscillators.

b. Use  $\nu = 10^{11} \text{ s}^{-1}$  and the partition function from problem set 2 to evaluate the mean-square fluctuation.

c. Compare  $\sigma_E$  to  $U = \langle E \rangle$ .

d. What happens as the temperature is raised?

e. What happens as the number of particles increases?

(Fluctuations are generally negligible relative to macroscopic quantities but are important for many processes under certain conditions, such as phase transitions.)

[Solution](#)

**15.29.** If the molecular partition function can be written as a product of factors,  $q = q_{tr} \cdot q_{int}$ , then energy, entropy and the other thermodynamic properties can be written as a sum of terms. Show that this is true for  $E$ ,  $S$  and  $A$ .

[Solution](#)

**15.30.** Calculate  $\frac{h^2}{8ma^2}$  for helium in a one-dimensional box of  $a=10 \text{ cm}$  and determine the energy level spacing for the first four levels. Compare this with  $k_B T$ . At what temperature are the energy levels spacing comparable in magnitude?

[Solution](#)

**15.31.** Calculate  $\Theta_v$  for  $\text{H}_2$  (frequency =  $4162 \text{ cm}^{-1}$ ) and  $\text{I}_2$  (frequency =  $213.1 \text{ cm}^{-1}$ ). Calculate  $q_v$  for these gases at  $300 \text{ K}$ .

[Solution](#)

**15.32.** Starting with the molecular partition function, prove for diatomic molecules in the high temperature limit that the translational, rotational and vibrational contributions to the heat capacity agree with the expression from equipartition.

[Solution](#)



**15.33.** Work out the heat capacity,  $C_v$ , at 300 K for the diatomic molecules listed below. Keep only the translational, rotational and vibrational motion. Use table below for the rotational and vibrational temperatures. Only use the high temperature approximation if it is valid. HCl, N<sub>2</sub>, O<sub>2</sub>, I<sub>2</sub>

	$q_{tr}$	$q_r$	$q_v$
HCl	High temp.	19.73	1.0000016
N <sub>2</sub>	High temp.	104.89	1.0000146
O <sub>2</sub>	High temp.	144.92	1.00059
I <sub>2</sub>	High temp.	555.5	1.552

[Solution](#)

**15.34.** The high temperature limit of the rotational partition function for diatomics is

$$q_r = \frac{T}{\sigma \Theta_r}$$

Give a brief explanation of the quantum mechanical origin of the symmetry number  $\sigma$ . Use equations where appropriate.

[Solution](#)

**15.35.** Prove that the Einstein function for the vibrational contribution to the heat capacity, Eq.(15.183) can be written as,

$$(C_V)_{Einstein} = R \left( \frac{u}{2} \coth \frac{u}{2} \right)^2$$

where

$$u = \frac{h\nu}{k_B T} = \frac{\Theta_v}{T}.$$

Show that the limiting value of Einstein function, Eq.(15.183), is the gas constant,  $R$ . (Recall that the Einstein vibration is restricted to one frequency only so this is consistent with equipartition that states at high temperatures the contribution to the heat capacity is equal to  $R$  for each degree of freedom. In this case, there is only one degree of freedom.)

[Solution](#)

### Partition Functions for Some Special Cases

**15.36.** Starting with Eq. (15.156) obtain an expression for the molar internal energy  $U_m$  of an ideal monatomic gas.

[Solution](#)

**15.37.** Calculate the molecular translational partition functions  $q_t$  for (a)  $N_2$ , (b)  $H_2O$ , (c)  $C_6H_6$  in a volume of  $1 \text{ m}^3$  at 300 K. In each case, calculate also  $\ln Q_{t,m}$ , where  $Q_{t,m}$  is the molar translational partition function.

[Solution](#)

**15.38.** The internuclear distance for  $N_2$  is 0.1095 nm. Determine the molecular rotational partition function  $q_r$  and  $\ln Q$  for  $N_2$  at 300 K.

[Solution](#)

**15.39.** Use the data in Table 15.3 (p. 807) to calculate, with reference to  $v = 0$ , the molecular vibrational partition function for  $CO_2$  at (a) 300 K and (b) 3000 K.

[Solution](#)

**15.40.** Expressions such as the Sackur-Tetrode equation for the entropy contain a term  $\ln(\text{constant} \times T)$ . At temperatures close to the absolute zero this term has large negative values, and the expression therefore leads to a negative value of the entropy. Comment on this.

[Solution](#)

**15.41.** Calculate the entropy of argon gas at 25 °C and 1 bar pressure.

[Solution](#)

**15.42.** From the data in Table 15.3, calculate, with reference to  $v = 0$ , the molecular vibrational partition function for  $\text{Br}_2$  at (a) 300 K and (b) 3000 K.

[Solution](#)

**15.43.** Give the symmetry numbers of the following molecules:  $\text{C}_3\text{O}_2$  (carbon suboxide),  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  in the staggered conformation,  $\text{C}_2\text{H}_6$  in the eclipsed conformation,  $\text{CHCl}_3$ ,  $\text{C}_3\text{H}_6$  (cyclopropane),  $\text{C}_6\text{H}_6$  (benzene),  $\text{NH}_2\text{D}$ ,  $\text{CH}_2\text{Cl}_2$ .

[Solution](#)

**15.44.** Show that the rotational partition function for a linear molecule can be expressed as

$$q_r = k_B T / \sigma B h$$

where  $B$  is the rotational constant defined by Eq.(13.63).

[Solution](#)

**\*15.45.** Calculate the molar translational entropy of chlorine gas at 25 °C and 0.1 bar pressure.

[Solution](#)

**\*15.46.** The carbon monoxide molecule has a moment of inertia of  $1.45 \times 10^{-46} \text{ kg m}^2$  and its vibrational frequency is  $6.50 \times 10^{13} \text{ s}^{-1}$ . Calculate the translational, rotational, and vibrational contributions to the molar entropy of carbon monoxide at 25 °C and 1 bar pressure.

[Solution](#)

- 15.47.** Suppose that a system has equally spaced energy levels, the separation between neighboring levels being  $\Delta\varepsilon$ . Prove that the fraction of the molecules in state  $i$ , having energy  $\varepsilon_i$  greater than the energy of the lowest level, is

$$1 - \exp\left(\frac{-\Delta\varepsilon}{k_B T}\right) \exp\left(\frac{-\varepsilon_i}{k_B T}\right)$$

What is the limiting value of this fraction as  $T \rightarrow \infty$ ? Explain your answer.

[Solution](#)

- \*15.48.** Deduce the following from the Sackur-Tetrode equation (Eq.(15.159)), which applies to an ideal monatomic gas:

- The dependence of entropy on relative molecular mass  $M_r$ ; also, obtain an expression for  $dS_m/dM_r$ .
- The dependence of heat capacity  $C_p$  on relative molecular mass.
- The dependence of entropy on temperature; also obtain an expression for  $dS_m/dT$ .

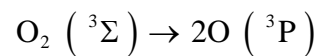
[Solution](#)

- \*15.49.** Molecules adsorbed on a surface sometimes behave like a two-dimensional gas. Derive an equation, analogous to the Sackur-Tetrode Eq. (15.159), for the molar entropy of such an adsorbed layer of atoms, in terms of the molecular mass  $m$  and the surface area  $A$ . What would be the molar entropy if  $10^{10}$  argon atoms were adsorbed on an area of  $1 \text{ cm}^2$  at  $25^\circ\text{C}$ ?

[Solution](#)

### Equilibrium constants

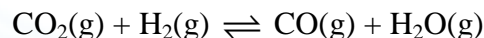
- 15.50.** Calculate the dissociation constant  $K_c$  for the reaction



at  $1\,000 \text{ K}$  expressing the answer in  $\text{mole l}^{-1}$ . Ignore nuclear degeneracy. Use the data from the table of Problem 51, along with the value  $\Lambda_o = 1.25 \times 10^{-9} \text{ cm}$ .

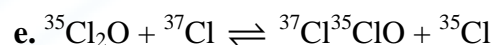
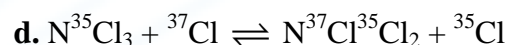
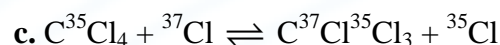
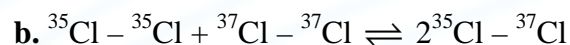
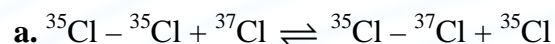
[Solution](#)

**15.51.** From the data in Table 15.5, calculate  $K_P$  at 1000 K for the “water-gas” reaction



[Solution](#)

**15.52.** Without making detailed calculations but by using symmetry numbers, estimate the equilibrium constants for the following reactions:



(Because of the similarity of the masses, these estimates will be quite accurate.)

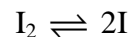
D. M. Bishop and K. J. Laidler, *J. Chem. Phys.*, 42, 1688(1965), have defined a *statistical factor* for a reaction as the number of equivalent ways in which a reaction can occur. Thus for reaction (a) from left to right the statistical factor is 2, since the  $^{37}\text{Cl}$  atom can abstract either of the two  $^{37}\text{Cl}$  atoms. For the reverse reaction the statistical factor  $r$  is 1, since the  $^{35}\text{Cl}$  atom can only abstract the  $^{35}\text{Cl}$  atom in order to give the desired products. If two identical molecules are involved, the statistical factor must be taken as the number of equivalent products divided by 2; thus for reaction (b) from right to left the statistical factor is  $\frac{1}{2}$ .

Bishop and Laidler proved that the ratio  $l/r$  of statistical factors is always equal to the ratio  $\sigma_A\sigma_B/\sigma_Y\sigma_Z$  of symmetry numbers. Verify that this is true for the given reactions.

This statistical factor procedure is useful in providing a simple insight into the factors that appear in equilibrium constants.

[Solution](#)

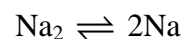
**\*15.53.** Calculate the equilibrium constant at 1000 °C for the dissociation



given the following information: moment of inertia of  $\text{I}_2 = 7.426 \times 10^{-45} \text{ kg m}^2$ , wavenumber for  $\text{I}_2$  vibration =  $213.67 \text{ cm}^{-1}$ ,  $\Delta U_0 = 148.45 \text{ kJ mol}^{-1}$ . The I atom is in a  $^2\text{P}_{3/2}$  state; neglect higher states.

[Solution](#)

**\*15.54.** Calculate the equilibrium constant  $K_P$  for the dissociation



at 1000 K, using the following data: internuclear separation in  $\text{Na}_2 = 0.3716 \text{ nm}$ , vibrational wavenumber  $\tilde{\nu} = 159.2 \text{ cm}^{-1}$ ,  $\Delta U_0 = 70.4 \text{ kJ mol}^{-1}$ . The Na atom is in a  $^2\text{S}_{1/2}$  state; neglect higher states.

[Solution](#)

**\*15.55.** Calculate the equilibrium constant  $K_P$  at 1200 K for  $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ , from the following data: internuclear separation in  $\text{Cl}_2 = 199 \text{ pm}$ , wavenumber for vibration =  $565.0 \text{ cm}^{-1}$ ,  $\Delta U_0 = 240.0 \text{ kJ mol}^{-1}$ . The ground state of Cl is a doublet,  $^2\text{P}_{\frac{3}{2}, \frac{1}{2}}$ , the

separation between the states being  $881 \text{ cm}^{-1}$ .

[Solution](#)

**15.56.** Calculate the isotopic ratio  $K_{\text{H}}/K_{\text{D}}$  at 300 K for the reactions



Take the zero-point energies of  $\text{H}_2$  and  $\text{D}_2$  to be  $26.1 \text{ kJ mol}^{-1}$  and  $18.5 \text{ kJ mol}^{-1}$ , respectively.

[Solution](#)

**Transition state theory**

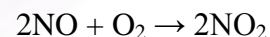
**15.57.** On the basis of transition-state theory, make rough estimates of the preexponential factors at 300 K for the following types of gas reactions:

- a. A bimolecular reaction between an atom and a diatomic molecule, with the formation of a linear activated complex.
- b. A bimolecular reaction between two diatomic molecules, the activated complex being nonlinear with one degree of restricted rotation.
- c. A bimolecular reaction between two nonlinear molecules, the activated complex being nonlinear with no restricted rotation.
- d. A trimolecular reaction between three diatomic molecules, the activated complex being nonlinear with one degree of restricted rotation.

Take the translational partition functions (for three degrees of freedom) to be  $10^{33} \text{ m}^{-3}$ , the rotational functions for each degree of freedom to be 10, the function for a restricted rotation to be 10, and the vibrational functions to be unity. Express the calculated preexponential factors in molecular units ( $\text{m}^3 \text{ s}^{-1}$ ) and in molar units ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

[Solution](#)

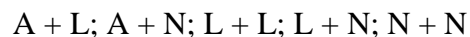
**15.58.** The rate constant for the reaction



has been found to be proportional to  $T^{-3}$ . Suggest an explanation for this behavior.

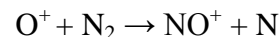
[Solution](#)

**15.59.** Deduce the temperature dependency of the preexponential factor of the following types of reactions, where A represents an atom, L a linear molecule, and N a nonlinear molecule:



[Solution](#)



**15.60.** The rate of the reaction

has been found over a certain temperature range to be proportional to  $T^{-0.5}$  (M. McFarland et al., *J. Chem. Phys.*, 59, 6620(1973). How can this be explained in terms of simple transition-state theory?

[Solution](#)

**15.61.** For the case of two atoms giving a product,  $\text{A} + \text{B} \rightleftharpoons [\text{AB}]^\ddagger \rightarrow \text{Product}$ , show that transition-state theory yields essentially the same expression for the rate constant as the collision theory expression of Eq. (9.76).

[Solution](#)

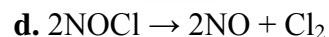
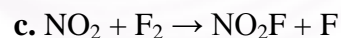
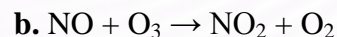
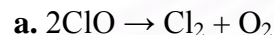
**15.62.** In mass-spectrometric experiments, P. Kebarle and coworkers (*J. Chem. Phys.*, 52, 212(1970) have found that under certain conditions the rate constant for the reaction



is proportional to  $T^{-2.5}$ . Suggest an explanation for this behavior.

[Solution](#)

**15.63.** On the basis of transition-state theory, and assuming the vibrational partitions to be temperature-independent, deduce the temperature dependence of the preexponential factor for each of the following reactions:

[Solution](#)



**15.64.** Benzaldehyde is oxidized by permanganate in aqueous solution. Suppose that the aldehydic hydrogen atom is replaced by a deuterium atom; what can be said on the basis of transition-state theory about the kinetic isotope ratio  $k_{\text{H}}/k_{\text{D}}$  at 25 °C? The wavenumber of the aldehydic C—H vibration is  $2900\text{ cm}^{-1}$ .

[Solution](#)

**15.65.** A transition-state theory study of the reaction  $\text{O}(^3\text{P}) + \text{HCl}$  generated the following information at  $T = 600\text{ K}$ :

*Reactants*

O	$q_t$	$1.767 \times 10^{32}\text{ m}^{-3}$	(for 3 degrees of freedom)
HCl	$q_t$	$6.084 \times 10^{32}\text{ m}^{-3}$	(for 3 degrees of freedom)
	$q_r$	39.40	(for 2 degrees of freedom)
	$\tilde{\nu}_0$	$2991.0\text{ cm}^{-1}$	

*Transition state (bent)*

	$q_t$	$1.050 \times 10^{33}\text{ m}^{-3}$	(for 3 degrees of freedom)
	$q_r$	1730	(for 3 degrees of freedom)
	$\tilde{\nu}_1$	$1407.9\text{ cm}^{-1}$	
	$\tilde{\nu}_2$	$266.8\text{ cm}^{-1}$	

The maximum of the reaction path is at  $45.97\text{ kJ mol}^{-1}$ . Calculate the rate constant at this temperature.

(*Note:* Some interesting problems on transition-state theory involving the use of a computer are to be found in S. J. Moss and C. J. Coady, *J. Chem. Ed.*, 60, 455(1983).)

[Solution](#)

**Essay questions**

- 15.66.** The molar entropy of a gas increases with the temperature and with the molecular weight. Give a physical explanation of these two effects.
- 15.67.** Explain the factors that influence the magnitudes of partition functions, and comment on the magnitudes of the molecular partition functions for translational, rotational, and vibrational energy. What characteristics of a molecule will lead to a high value of (a)  $q_t$ , (b)  $q_r$ , and (c)  $q_v$ ?
- 15.68.** Discuss the assumptions and limitations of conventional transition-state theory. Mention briefly procedures that have been used to overcome some of the limitations.
- 15.69.** On the basis of the treatment of equilibrium constants in terms of partition functions, explain the factors that account for the effects of isotopic substitution.

**Solutions**

**15.1.** Use Stirling's formula to calculate and approximate value for  $\ln(N!)$  and compare with the exact value for  $N=5, 10, 50, 100, 1,000$  and  $10,000!$

**Solution:**

Given: Stirling's formula, several values of  $N$ .

Required: calculate and approximate value for  $\ln(N!)$

We can use the Stirling's formula from Eq. 15.25 to solve for the approximate value of  $\ln(N!)$  :

$$\ln n! = n \ln n - n \quad \text{or} \quad n! = \frac{n^n}{e^n}$$

Note that the above formula works best if  $n$  is greater than 10.

$N$	exact $\ln(N!)$	stirling's formula	Error (%)
5	4.787492	3.047	36.35
10	15.10716	13.026	13.78
50	148.478	145.601	1.94
100	363.739	360.517	0.89
1000	5912.123	5907.755	0.07
10000	81959.46	82103.4	0.0018

$$Error = \frac{ABS(\ln(N!) - (N \ln N - N))}{\ln(N!)}$$

(Note:  $10,000!$  is considerably less than  $(6.023 \times 10^{23})!$  whence Stirling's formula is essentially exact.)

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**15.2.** The number of possible arrangements of 4 objects (A B C D) among 4 positions (do not list them).

**Solution:**

Given: 4 objects (A B C D)

Required: the number of possible arrangements

The four objects are distinguishable, so there are  $P_4^4 = 4! = 24$  arrangements.

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**15.3.** The number of possible arrangements of 3 objects (A B C) among 4 positions. List them all.

**Solution:**

Given: 3 objects (A B C)

Required: the number of possible arrangements among 4 positions

$$P_3^4 = \frac{4!}{(4-3)!} = 24$$

ABC_	AB_C	A_BC	_ABC
ACB_	AC_B	A_CB	_ACB
BAC_	BA_C	BAC_	_BAC
BCA_	BC_A	B_AC	_BAC
CAB_	CA_B	C_AB	_CAB
CBA_	CB_A	C_BA	_CBA

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**15.4.** Use the binomial distribution to work out the binomial coefficients for  $(x_1 + x_2)^n$  for  $n=5$ . Arrange the numbers in Pascal's triangle. Work out the quantities  $\binom{4}{3}$ ,  $\binom{5}{3}$  and  $\binom{5}{2}$  to check your entries.

**Solution:**

Given: see above

Required: binomial coefficients

$$(x_1 + x_2)^5 = x_1^5 + 5x_1^4x_2 + 10x_1^3x_2^2 + 10x_1^2x_2^3 + 5x_1x_2^4 + x_2^5$$

Work out Pascal's triangle:

$$\begin{array}{ccccccc} & & & & 1 & & \\ & & & 1 & 2 & 1 & \\ & & 1 & 3 & 3 & 1 & \\ & 1 & 4 & 6 & 4 & 1 & \\ 1 & 5 & 10 & 10 & 5 & 1 & \end{array}$$

Use  $C_r^n = \frac{P_r^n}{P_r^r} = \frac{n!}{(n-r)!r!} = \binom{n}{r}$  to check the entries and spot check Pascal's Triangle:  $\binom{4}{3} = 4$ ,  $\binom{5}{3} = 10$  and  $\binom{5}{2} = 10$  etc.

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**15.5.** Consider two sets of indistinguishable objects, {A A} and {B B B}. Work out and list the possible arrangements of these in 5 boxes, one object per box. Check your number against the formula.

$$P_r^{n!} = \frac{n!}{\prod_c n_c!}$$

**Solution:**

Given: {A A}, {B B B}, one object per box

Required: list all possible arrangements that can be placed in 5 boxes

$$P_r^{n!} = \frac{n!}{\prod_c n_c!} \rightarrow P_5^{5!} = \frac{5!}{3!2!} = 10$$

BBBAA  
AABBB  
BAABB  
BBAAB  
ABBBA

ABBAB  
BABBA  
ABABB  
BBABA  
BABAB

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**15.6.** Work out the number of ways that the three objects (A B C) can be placed in 5 boxes, no more than one object per box. List all the possibilities to confirm your number.

**Solution**

Given: (A B C), one object per box

Required: list all possible arrangements that can be placed in 5 boxes

$$P_n^m = \frac{m!}{(m-n)!} \rightarrow P_3^5 = \frac{5!}{(2)!} = 60$$

ABC\_ \_ A\_BC\_ \_ABC\_ A\_ \_BC AB\_ \_C AB\_C\_ A\_B\_C \_ \_ABC \_A\_B\_C \_AB\_C

Now permute each of these ten columns 6 times keeping the empty boxes straight, AS ABOVE:

ABC\_ \_      etc.  
ACB\_ \_  
BAC\_ \_  
BCA\_ \_  
CAB\_ \_  
CBA\_ \_

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- 15.7.** Work out the number of ways that the three objects (A A A) can be placed in 5 boxes, no more than one object per box. List all the possibilities to confirm your number.

$$C_r^n = \frac{n!}{(n-r)!r!}$$

**Solution:**

Given: (A A A), one object per box

Required: list all possible arrangements that can be placed in 5 boxes

$$C_r^n = \frac{n!}{(n-r)!r!} \rightarrow C_3^5 = \frac{5!}{(5-3)!3!} = 10$$

AAA\_\_  
\_AAA\_  
\_\_AAA  
\_A\_AA  
\_AA\_A

A\_\_AA  
A\_A\_A  
A\_AA\_  
AA\_\_A  
AA\_A\_

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**15.8.** Work out the number of ways that the two objects (A B) can be placed in 3 boxes with no restriction on the number of objects per box. List all the possibilities to confirm your number.

**Solution:**

Given: (A B), no restriction on the number of objects per box

Required: list all possible arrangements that can be placed in 3 boxes

$$N = m^n \rightarrow 3^2 = 9$$

<u>AB</u> _ _	_ AB
_ <u>AB</u> _	B _ A
_ _ <u>AB</u>	B A _
A _ B	_ B A
A B _	

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**15.9.** Work out the number of ways that the two objects (A A) can be placed in 4 boxes without restriction on the number of objects per box. List all the possibilities to confirm your number.

**Solution:**

Given: (A A), no restriction on the number of objects per box

Required: list all possible arrangements that can be placed in 4 boxes

$$N = \frac{(m+n-1)!}{n!(m-1)!} \rightarrow \frac{(4+2-1)!}{2!3!} = 10$$

$\underline{AA}$  \_ \_ \_  
 \_  $\underline{AA}$  \_ \_  
 \_ \_  $\underline{AA}$  \_  
 \_ \_ \_  $\underline{AA}$   
 A A \_ \_

\_ A A \_  
 \_ \_ A A  
 A \_ A \_  
 A \_ \_ A  
 \_ A \_ A

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**15.10.** When we remove the condition of distinguishability from the  $n$  objects of Eq.(A.5), we divide by  $n!$  to obtain Eq.(A.6). By considering the simple case of 2 objects and 3 boxes, (same as Problem 15.8) show that it is improper similarly to divide Eq.(A.7) by  $n!$  to obtain the desired result for Eq.(A.8).

**Solution:**

Given: 2 objects, 3 boxes

Required: see above

$$N = P_n^m = \frac{m!}{(m-n)!} \text{ Eq.(A.5) for distinguishable} \rightarrow \frac{m!}{(m-n)!n!} \text{ Eq.(A.6) for indistinguishable}$$

Can we do the same for:

$$\text{Eq.(A.7) } N = m^n \text{ for distinguishable} \rightarrow N = \frac{m^n}{n!} \text{ for indistinguishable?}$$

$$\text{The answer is no. We must use: } N = \frac{(m+n-1)!}{n!(m-1)!}$$

Show this for the case of 2 objects and 3 boxes:

$$\text{Wrong: } N = \frac{m^n}{n!} \rightarrow \frac{3^2}{2!} = 4.5$$

$$\text{Correct: } N = \frac{(m+n-1)!}{n!(m-1)!} \rightarrow \frac{(3+2-1)!}{2!(3-1)!} = 6$$

AA \_  
\_ AA \_  
\_ \_ AA

A \_ A  
\_ A A  
A A \_

It will be seen from this problem that  $m^n/n!$  is a number lying between  $m!/(n!(m-n)!)$  (Eq.(A.6) and  $(m+n-1)!/n!(m-1)!$ , Eq.(A.8). When arrangements that differ between the two ways of counting, (due to distinguishability), represent a negligible part of the total number of arrangements, the difference between the ways of counting becomes unimportant.

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**15.11.** A partially deuterated methane sample is analyzed and found to contain equal molar quantities of hydrogen and deuterium. On a random basis, calculate the percentage of species  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ ,  $\text{CHD}_3$ ,  $\text{CD}_4$ .

**Solution:**

Given: see above

Required: calculate % of species  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ ,  $\text{CHD}_3$ ,  $\text{CD}_4$  on a random basis.

Let the probability of an H appearing by  $P_H$  and a D appearing as  $P_D$ . These probabilities are take as equal and  $P_H = P_D = 0.5$ .

There can be up to 4 bonds, so we have:

$$(P_H + P_D)^4 = P_H^4 + 4P_H^3P_D^1 + 6P_H^2P_D^2 + 4P_H^1P_D^3 + P_D^4$$

The chance of 4 H is

$$P_H^4 = 1/16$$

The chance of 3 H and 1 D is

$$4P_H^3P_D^1 = 1/4$$

The chance of 2 H and 2 D is

$$6P_H^2P_D^2 = 6/16 = 3/8$$

The chance of 1 H and 3 D is

$$4P_H^1P_D^3 = 1/4$$

The chance of 4 D is

$$P_D^4 = 1/16$$

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**15.12.** Show that  $\ln \left[ \frac{m!}{n!(m-n)!} \right]$  and  $\ln \left[ \frac{(m+n-1)!}{n!(m-1)!} \right]$  both approach  $\ln \left[ \frac{m^n}{n!} \right]$  as  $n$  becomes large, provided that  $m \gg n$ . (Use Stirling's formula and use the fact that  $m \gg n$ , and  $m \gg 1$ .)

**Solution:**

Given: see above

Required: see above

$$\begin{aligned} \ln \left[ \frac{m!}{n!(m-n)!} \right] &= \ln \left[ \frac{m(m-1)(m-2)\dots(m-n+1)}{n!} \right] \\ \rightarrow \lim_{n \rightarrow \infty} \ln \left[ \frac{m(m-1)(m-2)\dots(m-n+1)}{n!} \right] &= \ln \left[ \frac{m(m-1)(m-2)\dots(m-n)}{n!} \right] \\ \Rightarrow \ln \left[ \frac{\overbrace{m \cdot m \cdot m \dots m}^{n \text{ times}}}{n!} \right] &= \ln \left[ \frac{m^n}{n!} \right] \end{aligned}$$

and

$$\begin{aligned} \ln \left[ \frac{(m+n-1)!}{n!(m-1)!} \right] &= \ln \left[ \frac{(m+n-1)(m+n-2)\dots(m-2)\cancel{(m-1)!}}{n!\cancel{(m-1)!}} \right] \\ &= \lim_{\substack{n \rightarrow \infty \\ m \gg n}} \ln \left[ \frac{\overbrace{(m+n-1)(m+n-2)\dots(m-2)}^{n-2 \text{ terms}}}{n!} \right] = \ln \left[ \frac{m^{n-2}}{n!} \right] \\ &\xrightarrow[n \rightarrow \infty]{m \gg n} \ln \left[ \frac{m^n}{n!} \right] \end{aligned}$$

Alternately we can start with Eqs.(15.56) and (15.59) to obtain Eq.(15.60):

$$\ln \Omega_{BE} = \sum_j \left[ +g_j \ln \left( 1 + \frac{N_j}{g_j} \right) + N_j \ln \left( \frac{g_j}{N_j} + 1 \right) \right]$$

$$\ln \Omega_D = \sum_j \left[ \pm g_j \ln \left( 1 \pm \frac{N_j}{g_j} \right) + N_j \ln \left( \frac{g_j}{N_j} \pm 1 \right) \right]$$

$$\xrightarrow{g_j \gg N_j} \sum_j \left[ N_j + N_j \ln \left( \frac{g_j \pm N_j}{N_j} \right) \right]$$

$$= \sum_j \left[ N_j + N_j \ln (g_j \pm N_j) - N \ln (N_j) \right]$$

We have used:  $g_j \ln \left( 1 \pm \frac{N_j}{g_j} \right) \cong \pm N_j$  by expanding the natural logarithm,  $\ln(1 \pm x) \cong \pm x$  for small  $x$ . Once again, neglect  $g_j$  relative to  $N_j$  which gives Eq2.(15.60) and (15.61),

$$\ln \Omega_D = \sum_j \left[ N_j \ln (g_j) - N_j \ln (N_j) + N_j \right]$$

This result is of tremendous importance in permitting us to ignore the restrictions of Bose-Einstein and Fermi-Dirac quantum statistics when the number of accessible quantum states (the  $m$  boxes) far exceed the number of molecules (the  $n$  objects).

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**15.13.** Show that the maximum entropy,  $S$ , is obtained when all the probabilities,  $p_i$  are equal, where

$$S = -\sum_{i=1}^n p_i \ln p_i \quad \text{and} \quad \sum_{i=1}^n p_i = 1$$

(This shows us that complete lack of knowledge of which state the system is in results in the highest entropy. When all states are equally likely, we have no preferential state, and this means the most random or highest entropy.)

**Solution:**

Given: see above

Required: prove the above expression for equal probabilities

To solve for this problem, we can use the Lagrange multipliers. Take the derivative with respect to each probability subject to the condition,  $\sum_{i=1}^n p_i = 1$ . For maximum entropy, we set the results equal to zero:

$$\left( \frac{\partial S}{\partial p_i} \right)_{p_j, j \neq i} = -\ln p_i - 1 + \alpha = 0$$

$$+\ln p_1 = \alpha - 1$$

so,  $+\ln p_2 = \alpha - 1$  hence all the  $p_i$ 's must be equal and  $p_i = \exp(\alpha - 1)$

$$+\ln p_3 = \alpha - 1$$

Since  $\sum_{i=1}^n p_i = 1$  then

$$1 = \sum_{i=1}^n p_i = \sum_{i=1}^n \exp(\alpha - 1) = \exp(\alpha - 1) \sum_{i=1}^n 1 = n \exp(\alpha - 1)$$

so

$$\ln\left(\frac{1}{n}\right) = \alpha - 1 \text{ so } \boxed{p_i = \frac{1}{n}}$$

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**15.14.** Prove that for an  $N$  particle quantum state, the wave function must be either odd or even under the permutation of any two of the  $N$  particles.

(This symmetry, of course, distinguishes bosons from fermions.)

**Solution:**

Given:  $N$  particle quantum state

Required: prove the above

Let  $\Psi(1, 2, 3, \dots, N)$  be an  $N$  particle state. Now permute two particles:

$$P_{ij}\Psi(1, 2, 3, \dots, j \dots i \dots N) = a\Psi(1, 2, 3, \dots, j \dots i \dots N)$$

but two permutations must get us back to the same state that we started from,

$$P_{ij}P_{ij}\Psi(1, 2, 3, \dots, j \dots i \dots N) = a^2\Psi(1, 2, 3, \dots, j \dots i \dots N)$$

The only way this can happen is if  $a^2 = 1$  or  $a = \pm 1$ .

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**15.15.** A more accurate form of Stirling's approximation is

$$\ln N! = N \ln N - N + \ln \sqrt{2\pi N}$$

In the stopcock opening and closing example, recalculate the effect of  $\Delta S_{II \rightarrow III}$  using the above approximation and show that the entropy change is negligible compared to  $\Delta S_{I \rightarrow II}$ . Assume that the two volumes are equal, and consider what happens to this new entropy change  $\Delta S_{II \rightarrow III} < 0$  as the number of particles goes to infinity

(Although we observe no noticeable change when we physically close the stopcock in going from state II to III, there is a change due to our definition. This problem asks you to look into. The reason the change is negligible from our theory is because we are dealing with an enormous number of particles, and can use Stirling's approximation. However, if we had only a few particles, then the effect of closing the stopcock would lead to a difference between the two states, II and III, i.e. the "entropy" would show a decrease. This underscores the fact that we can not define entropy for a small number of particles because entropy is a statistical quantity.)

**Solution:**

Given: altered version of Stirling's approximation

Required: the effect of  $\Delta S_{II \rightarrow III}$

The expression from the notes using the usual form of Stirling's approximation is:

$$\begin{aligned} \Delta S_{II \rightarrow III} &= A \ln \left\{ \frac{(N_1)^{N_1} (N_2)^{N_2} (N_1 + N_2)!}{(N_1 + N_2)^{N_1 + N_2} N_1! N_2!} \right\} \\ &= A \left\{ N_1 \ln N_1 + N_2 \ln N_2 + (N_1 + N_2) \ln (N_1 + N_2) - N_1 - N_2 \right. \\ &\quad \left. - (N_1 + N_2) \ln (N_1 + N_2) - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2 \right\} = 0 \end{aligned}$$

We note that all the terms cancel. If we use the better approximation for Stirling's approximation,

$$\ln N! = N \ln N - N + \ln \sqrt{2\pi N}$$

we get:

$$\begin{aligned} \Delta S_{II \rightarrow III} &= A \ln \left\{ \frac{(N_1)^{N_1} (N_2)^{N_2} (N_1 + N_2)!}{(N_1 + N_2)^{N_1 + N_2} N_1! N_2!} \right\} \\ &= A \left\{ N_1 \ln N_1 + N_2 \ln N_2 + (N_1 + N_2) \ln (N_1 + N_2) - N_1 - N_2 + \ln \sqrt{2\pi (N_1 + N_2)} \right. \\ &\quad \left. - (N_1 + N_2) \ln (N_1 + N_2) - N_1 \ln N_1 + N_1 - \ln \sqrt{2\pi N_1} - N_2 \ln N_2 + N_2 - \ln \sqrt{2\pi N_2} \right\} \\ &= A \ln \sqrt{\frac{(N_1 + N_2)}{2\pi N_1 N_2}} \end{aligned}$$

Let us assume that  $V_1 = V_2$ , so  $N_1 = N_2 = N/2$  giving

$$A \ln \sqrt{\frac{(N_1 + N_2)}{2\pi N_1 N_2}}^{N_1 = N_2} = A \ln \sqrt{\frac{(2N/2)}{2\pi (N/2)^2}} = \frac{A}{2} \ln \frac{2N}{\pi N^2} = \frac{A}{2} \ln \frac{2}{\pi N}$$

write this as:  $\frac{A}{2} \ln \frac{2}{\pi N} = \frac{A}{2} \left( \ln \frac{2}{\pi} - \ln N \right)$

This shows that there is a decrease in entropy for large  $N$ , but this is negligible. The correction from this shows a decrease in entropy of  $-A \ln N$  when the stopcock is closed. If we plug in  $A=k$ , then we get

$$-A \ln N = -k \ln N = -(1.38 \times 10^{-23}) \ln(6.23 \times 10^{23}) = -(1.38 \times 10^{-23}) 55 = -7.6 \times 10^{-22}$$

which is negligible. Suppose we had  $10^{10}$  moles, the calculation would change to:

$$-A \ln N = -k \ln N = -(1.38 \times 10^{-23}) \ln(6.23 \times 10^{33}) = -(1.38 \times 10^{-23}) 78 = -10.7 \times 10^{-22}$$

which is still negligible.

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**15.16.** Using:  $\frac{N_1}{V_1} = \frac{N_2}{V_2}$  prove the relationship:

$$\ln \left[ \frac{(V_1/V_c)^{N_1} (V_2/V_c)^{N_2} (N_1 + N_2)!}{\left( (V_1/V_c)^{N_1} + (V_2/V_c)^{N_2} \right) (N_1)! (N_2)!} \right] = \ln \left[ \frac{(N_1)^{N_1} N_2^{N_2} (N_1 + N_2)!}{(N_1^{N_1} + N_2^{N_2}) (N_1)! (N_2)!} \right]$$

**Solution:**

Given:  $\frac{N_1}{V_1} = \frac{N_2}{V_2}$

Required: prove the above relationship

Cancel the  $V_c$ 's:

$$\begin{aligned} \ln \left[ \frac{(V_1/V_c)^{N_1} (V_2/V_c)^{N_2} (N_1 + N_2)!}{(V_1/V_c + V_2/V_c)^{N_1+N_2} N_1! N_2!} \right] &= \ln \left[ \left( \frac{V_c^{N_1+N_2}}{V_c^{N_1} V_c^{N_2}} \right) \frac{(V_1)^{N_1} (V_2)^{N_2} (N_1 + N_2)!}{(V_1 + V_2)^{N_1+N_2} N_1! N_2!} \right] \\ &= \ln \left[ \frac{(V_1)^{N_1} (V_2)^{N_2} (N_1 + N_2)!}{(V_1 + V_2)^{N_1+N_2} N_1! N_2!} \right] \end{aligned}$$

Now consider only the powers (since the factorials remain):

$$\ln \left[ \frac{(V_1)^{N_1} (V_2)^{N_2}}{(V_1 + V_2)^{N_1+N_2}} \right] = N_1 \ln V_1 + N_2 \ln V_2 - (N_1 + N_2) \ln (V_1 + V_2)$$

Use  $N_1 V_2 = N_2 V_1$  to get

$$= N_1 \ln V_1 + N_2 \ln V_2 - (N_1 + N_2) \ln \left( \frac{N_1^2 V_2 + N_2^2 V_1}{N_1 N_2} \right)$$

Now write out all the terms as a sum of  $\ln$ 's:

$$= N_1 \ln V_1 + N_2 \ln V_2 - (N_1 + N_2) \ln (N_1^2 V_2 + N_2^2 V_1) + N_1 \ln N_1 + N_1 \ln N_2 \\ + N_2 \ln N_1 + N_2 \ln N_2$$

Now we can use the fact that  $N_1 V_2 = N_2 V_1$  to get

$$= N_1 \ln V_1 + N_2 \ln V_2 - (N_1 + N_2) \ln (N_1 V_2 \{N_1 + N_2\}) + N_1 \ln N_1 + N_1 \ln N_2 \\ + N_2 \ln N_1 + N_2 \ln N_2$$

and expand the terms:

$$= N_1 \ln V_1 + N_2 \ln V_2 - (N_1 + N_2) \ln (N_1 V_2) - (N_1 + N_2) \ln (N_1 + N_2) \\ + N_1 \ln N_1 + N_1 \ln N_2 + N_2 \ln N_1 + N_2 \ln N_2 \\ = N_1 \ln V_1 + N_2 \ln V_2 - (N_1 + N_2) \ln (N_1) - (N_1 + N_2) \ln (V_2) - (N_1 + N_2) \ln (N_1 + N_2) \\ + N_1 \ln N_1 + N_1 \ln N_2 + N_2 \ln N_1 + N_2 \ln N_2 \\ = N_1 \ln V_1 + N_2 \ln V_2 - N_1 \ln N_1 - N_2 \ln N_1 - N_1 \ln V_2 - N_2 \ln V_2 - (N_1 + N_2) \ln (N_1 + N_2) \\ + N_1 \ln N_1 + N_1 \ln N_2 + N_2 \ln N_1 + N_2 \ln N_2$$

collect and cancel terms:



$$\begin{aligned}
&= N_1 \ln V_1 + \cancel{N_2 \ln V_2} - \cancel{N_1 \ln N_1} - \cancel{N_2 \ln N_1} - N_1 \ln V_2 - \cancel{N_2 \ln V_2} - (N_1 + N_2) \ln (N_1 + N_2) \\
&+ \cancel{N_1 \ln N_1} + N_1 \ln N_2 + \cancel{N_2 \ln N_1} + N_2 \ln N_2 \\
&= N_1 \ln V_1 - N_1 \ln V_2 + N_1 \ln N_2 + N_2 \ln N_2 - (N_1 + N_2) \ln (N_1 + N_2) \\
&= N_1 \ln \left( \frac{V_1}{V_2} \right) + N_1 \ln N_2 + N_2 \ln N_2 - (N_1 + N_2) \ln (N_1 + N_2)
\end{aligned}$$

Using  $\frac{V_1}{V_2} = \frac{N_1}{N_2}$

$$\begin{aligned}
&= N_1 \ln \left( \frac{N_1}{N_2} \right) + N_1 \ln N_2 + N_2 \ln N_2 - (N_1 + N_2) \ln (N_1 + N_2) \\
&= N_1 \ln N_1 - N_1 \ln N_2 + N_1 \ln N_2 + N_2 \ln N_2 - (N_1 + N_2) \ln (N_1 + N_2) \\
&= N_1 \ln N_1 - \cancel{N_1 \ln N_2} + \cancel{N_1 \ln N_2} + N_2 \ln N_2 - (N_1 + N_2) \ln (N_1 + N_2) \\
&= N_1 \ln N_1 + N_2 \ln N_2 - (N_1 + N_2) \ln (N_1 + N_2) \\
&= \ln \left[ \frac{N_1^{N_1} N_2^{N_2}}{(N_1 + N_2)^{N_1 + N_2}} \right]
\end{aligned}$$

which is in the form we want.

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**15.17.** Without considering energy, calculate the statistical weights for 30 quanta distributed amongst 30 oscillators for the following distributions of the quanta:

$$N_0 = 0, N_1 = 30, N_{2 \rightarrow 29} = 0$$

$$N_0 = 1, N_1 = 28, N_2 = 1, N_{3 \rightarrow 29} = 0$$

$$N_0 = 10, N_1 = 10, N_2 = 10, N_{3 \rightarrow 29} = 0$$

(This is a problem of combinatorics, how many ways can 30 indistinguishable objects be distributed between 30 levels. For oscillators, we usually label the lowest state by a “0”, so we go up to the 29<sup>th</sup> level. In general, there is usually degeneracy (more than one state with the same energy) Here we are calculating the degeneracy for various possible energies. In case a) the energy is  $30\varepsilon_1$ , for b) the energy is  $\varepsilon_0 + 28\varepsilon_1 + 2\varepsilon_2$  and for c)  $10\varepsilon_0 + 10\varepsilon_1 + 10\varepsilon_2$ . The problem calculates the number of ways (the statistical weight) that indistinguishable quantum can be arranged to give that particular energy.)

**Solution:**

Given: see above

Required: statistical weights

The number of ways of producing the energies of these distributions is simply:

$$\frac{N!}{\prod_{i=1}^{30} N_i}$$

a.  $N_0 = 0, N_1 = 30, N_{2 \rightarrow 29} = 0$

$$\frac{N!}{\prod_{i=1}^{30} N_i} \rightarrow \frac{30!}{0! 30! 0! \dots 0!} = \boxed{1}$$

b.  $N_0 = 1, N_1 = 28, N_2 = 1, N_{3 \rightarrow 29} = 0$

$$\frac{N!}{\prod_{i=1}^{30} N_i} \rightarrow \frac{30!}{1! \cdot 28! \cdot 1! \cdot \dots \cdot 0!} = 30 \cdot 29 = \boxed{870}$$

c.  $N_0 = 10, N_1 = 10, N_2 = 10, N_{3 \rightarrow 29} = 0$

$$\frac{N!}{\prod_{i=1}^{30} N_i} \rightarrow \frac{30!}{10! \cdot 10! \cdot 10! \cdot \dots \cdot 0!} = 29 \cdot 26 \cdot 23 \cdot 22 \cdot 21 \cdot 19 \cdot 17 \cdot 13 \cdot 11 \cdot 5 = \boxed{1.8503323 \times 10^{12}}$$

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**15.18.** Show that Eq.(15.148) satisfies FD and BE conditions of respectively no more than 1 particle, on the average, in a state, and any number of particles in a state. Let  $x = \exp \left[ (\varepsilon_\alpha - \mu') / k_B T \right]$

**Solution:**

Given:  $x = \exp \left[ (\varepsilon_\alpha - \mu') / k_B T \right]$

Required: show above statement

The expression for BE (-) statistics and FD (+) statistic is

$$\frac{1}{\exp \left[ (\varepsilon_\alpha - \mu') / k_B T \right] \mp 1} = \frac{1}{e^x \mp 1} \equiv Z^{\text{BE}}_{\text{FD}}(x)$$

Since the range of  $x$  is  $\pm \infty$ , we have for FD statistics, (+) sign:

$$Z^{\text{FD}}(-\infty) = 1; \quad Z^{\text{FD}}(0) = 1/2; \quad Z^{\text{FD}}(\infty) = 0;$$

For BE statistics, (-) sign:

$$Z^{\text{BE}}(-\infty) = 1; \quad Z^{\text{BE}}(0) = \infty; \quad Z^{\text{BE}}(\infty) = 0;$$

Hence the average population of an eigenstate for fermions cannot exceed 1 while there is no restriction on the average population of an eigenstate for bosons.

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**15.19.** Starting from

$$S = k_B \ln \Omega(E, V, N)$$

obtain the equation:

$$PV = k_B T \ln \Xi(T, V, \mu)$$

where  $\Xi(T, V, \mu)$  is the grand partition function. Do NOT derive the ideal gas law (i.e. do not assume the particles do not interact).

(The grand partition function is one that is commonly used in chemical reactions.)

**Solution:**

Given:  $S = k_B \ln \Omega(E, V, N)$

Required: derive  $PV = k_B T \ln \Xi(T, V, \mu)$

Grand Canonical ensemble: change variable  $N$  to  $\mu$ , and  $E$  to  $T$ :

We have already changed the variables from  $S = k \ln \Omega(E, V, N)$ , see Eq.(15.107),  $E$  to  $T$ , giving  $-A/T$ , so now, using the Legendre transformation,

$$-\frac{A}{T} = k_B \ln Q(T, V, N) \rightarrow$$

$$\Phi(T, V, \mu) = \left[ -\frac{A}{T} - \left( \frac{\partial(-A/T)}{\partial N} \right)_{T, V, \mu} N \right] = \left[ -\frac{A}{T} + \frac{1}{T} \left( \frac{\partial A}{\partial N} \right)_{T, V, \mu} N \right] = -\frac{A}{T} + \frac{1}{T} \mu N$$

Following the same procedure, we get,

$$k \ln \Xi(T, V, \mu) = \Phi(T, V, \mu) = -\frac{A}{T} + \frac{1}{T} \mu N = -\frac{E}{T} + S + \frac{\mu}{T} N$$

To identify the function that is natural for the grand canonical ensemble, note that the Gibbs energy for a one-component system is,

$$G = N\mu = H - TS = E + PV - TS \quad (\text{a})$$

divide by  $T$  and rearrange,

$$N \frac{\mu}{T} = \frac{E}{T} + \frac{PV}{T} - S \quad (\text{b})$$

Comparing Eq.(a) with Eq.(b) shows that,

$$\frac{PV}{T} = k_B \ln \Xi(T, V, \mu)$$

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**15.20.** Derive expressions for the energy  $U=E$ , the entropy  $S$  the pressure  $P$  and the Helmholtz energy  $A$ , and the Gibbs energy  $G$  in terms of the Canonical ensemble,  $Q$ .

**Solution:**

Given:  $U = E, S, P, A, G, Q$

Required: derivation

We have:

$$A = -k_B T \ln Q(T, V, N)$$

and

$$dA = -Sdt - PdV$$

using

$$\left( \frac{\partial A}{\partial V} \right)_T = -P \qquad \left( \frac{\partial A}{\partial T} \right)_V = -S$$

gives

$$S = -\left( \frac{\partial A}{\partial T} \right)_V = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_V + k_B \ln Q$$

$$P = \left( \frac{\partial A}{\partial V} \right)_T = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_T$$

and from  $A=E-TS$

$$E = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V$$

finally the Gibbs energy is

$$G = A + PV = -k_B T \ln Q + k_B T V \left( \frac{\partial \ln Q}{\partial V} \right)_T$$

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**15.21.** Find the natural function for the isothermal-isobaric ensemble,  $\Delta(T, P, N)$ , i.e. for variables  $T, P$  and  $N$ .

**Solution:**

Given: isothermal-isobaric

Required: natural function

We have:

$S = k_B \ln \Omega(U, V, N) = \Phi(U, V, N)$	microcanonical ensemble
$\rightarrow \Phi(T, V, N) = k_B \ln \Omega(T, V, N) \equiv k \ln Q(T, V, N)$	canonical ensemble
$\rightarrow \Phi(T, V, \mu) = k_B \ln \Omega(T, V, \mu) \equiv k \ln \Xi(T, V, \mu)$	grand canonical ensemble
$\rightarrow \Phi(T, P, N) = k_B \ln \Omega(T, P, N) \equiv k \ln \Delta(T, P, N)$	isothermal-isobaric ensemble

We know that the natural function of the variables  $T, V, N$  is  $-A/T$ , so all we have to do is apply the Legendre transformation for  $V$  to  $T$ ,

$$\begin{aligned}\Phi(T, P, N) &= -\frac{A}{T} - \left( \frac{\partial(-A/T)}{\partial P} \right)_{T, V, N} P = -\frac{A}{T} + \frac{1}{T} \left( \frac{\partial A}{\partial P} \right)_{T, V} P \\ &= -\frac{A}{T} - \frac{1}{T} VP = -\left( \frac{A + PV}{T} \right) = -\frac{G}{T}\end{aligned}$$

so, as no surprise the isothermal-isobaric ensemble is

$$\boxed{\Phi(T, P, N) = -\frac{G}{T} = k_B \ln \Omega(T, P, N) \equiv k_B \ln \Delta(T, P, N)}$$

or

$$\boxed{G = -k_B T \ln \Delta(T, P, N)}$$

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**15.22.** Obtain an expression for  $C_p$  in terms of the partition function  $Q$  for the system.

**Solution:**

Given:  $C_p, Q$

Required: see above

We know that  $C_p = \left( \frac{\partial H}{\partial T} \right)_p$ ,

and that  $H - U_0 = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_v + N k_B T$

if  $U_0 = 0$ , substitution of the above expression into the expression for  $C_p$  will yield:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

$$C_p = \left( \frac{\partial \left[ k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_v + N k_B T \right]}{\partial T} \right)_p$$

$$C_p = \left\{ \frac{\partial}{\partial T} \left[ k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_v \right] \right\}_p + N k_B$$

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**15.23.** Obtain an expression for the pressure  $P$  in terms of the molecular partition function  $q$ , for (a) distinguishable molecules and (b) indistinguishable molecules. Express the result in terms of the number of molecules  $N$  and also the amount of substance  $n$ .

**Solution:**

Given:  $P, q, N, n$

Required: see above

From Eq. 3.118,

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T$$

**a.** From Eq. 15.45 for distinguishable molecules

$$Q = q^N$$

Take the natural logarithm on both sides yield:

$$\ln Q = N \ln q$$

Therefore,

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$P = k_B T \left(\frac{\partial (N \ln q)}{\partial V}\right)_T$$

$$P = k_B T \left(\frac{\ln q \partial N + N \partial \ln q}{\partial V}\right)_T$$

$$P = N k_B T \left(\frac{\partial \ln q}{\partial V}\right)_T$$

$$\boxed{P = nRT \left(\frac{\partial \ln q}{\partial V}\right)_T}$$

b. From Eq. 15.47 for indistinguishable molecules,

$$Q = \frac{q^N}{N!}$$

Take the natural logarithm on both sides yield:

$$\ln Q = \ln q^N - \ln N!$$

$$\ln Q = N \ln q - N \ln N + N$$

Similarly to **a.**, we will substitute the above expression into  $P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_T$ , and will yield the same answer as **a.**:

$$\boxed{P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_T}$$

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**15.24.** The partition function for each degree of vibrational freedom is  $1 / \left[ 1 - \exp \left( \frac{-h\nu}{k_B T} \right) \right]$  (Eq.(15.173)). Obtain from this expression the limiting value of the vibrational contribution to  $C_V$  as  $T$  approaches infinity.

**Solution:**

Given:  $1 / \left[ 1 - \exp \left( \frac{-h\nu}{k_B T} \right) \right], T \rightarrow \infty$

Required: limiting value of the vibrational contribution to  $C_V$

In the limit as  $T \rightarrow \infty$  the vibrational partition function becomes

$$\frac{1}{1 - \left( 1 - \frac{h\nu}{k_B T} \right)} = \frac{k_B T}{h\nu}$$

Then

$$U_m - U_{0,m} = RT$$

and

$$C_{V,m} = R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

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**15.25.** Chemical reactions often lead to the formation of products whose energy distributions show significant deviations from the statistical distribution of Eq. 15.40. In a study of an elementary reaction with  $^{16}\text{O}^1\text{H}$  radical as one of the products [Zhang, van der Zande, Bronikowski, and Zare, *J. Chem. Phys.* 94, 2704(1994)], the following rotational distribution was observed for the  $\text{OH}(\nu = 0)$  state (normalized such that  $\sum n_J/N = 1$ ). Compare this to the statistical distribution expected from Eq.(15.84) at 298 K. The equilibrium bond distance of OH is 0.96966 Å.

$J$	7	8	9	10	11	12	13
$n_J/N$	0.0181	0.0232	0.0356	0.0475	0.0377	0.0762	0.1045
$J$	14	15	16	17	18	19	20
$n_J/N$	0.1266	0.1459	0.1466	0.1306	0.0907	0.0167	0.0000

**Solution:**

Given:  $\nu = 0$ ,  $\sum n_J/N = 1$ ,  $T = 298 \text{ K}$ ,  $d_{\text{OH}} = 0.96966 \text{ Å}$

Required: comparison to statistical distribution

The reduced mass of  $^{16}\text{O}^1\text{H}$  is

$$\mu = \frac{1.0078 \cancel{\text{ g mol}^{-1}} \times 15.9949 \cancel{\text{ g mol}^{-1}}}{(1.0078 + 15.9949) \cancel{\text{ g mol}^{-1}}} \cdot \frac{1}{6.022 \times 10^{23} \cancel{\text{ mol}^{-1}}} \cdot \frac{\text{kg}}{1000 \cancel{\text{ g}}}$$

$$\mu = 1.574\,335\,324 \times 10^{-27} \text{ kg}$$

The moment of inertia is

$$I = (1.574\,335\,324 \times 10^{-27} \text{ kg}) (0.96966 \times 10^{-10} \text{ m})^2 = 1.480\,253\,857 \times 10^{-47} \text{ kg m}^2$$

The rotational partition function is

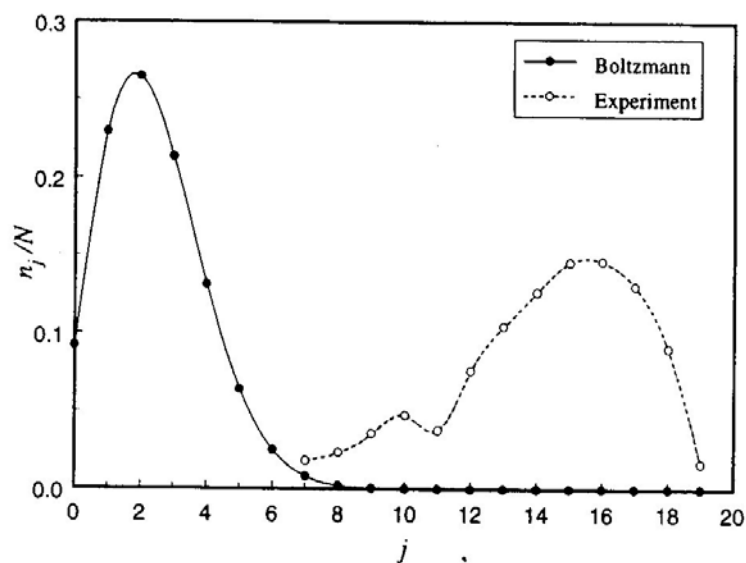
$$q_r = \frac{2Ik_{\text{B}}T}{h^2} = \frac{2(1.480\,253\,857 \times 10^{-47} \cancel{\text{ kg m}^2}) (1.381 \times 10^{-23} \cancel{\text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}}) (298 \cancel{\text{ K}})}{(6.626 \times 10^{-34})^2 \cancel{\text{ m}^4 \text{ kg}^2 \text{ s}^{-2}}}$$

$$q_r = 0.277\,506\,523 \text{ at } T = 298 \text{ K}$$

Now, using Eq. 15.40 with  $g_J = 2J + 1$ , and  $\epsilon_J = \frac{J(J+1)\hbar^2}{2I}$ , we write

$$\frac{n_J}{N} = \frac{2J+1}{q_r} \exp\left[\frac{-J(J+1)\hbar^2}{2Ik_B T}\right].$$

A plot of this fraction as a function of  $J$  along with the experimental distribution is shown in the accompanying figure.



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- 15.26.** Suppose that an array of harmonic oscillators has common frequency of  $\nu = 10^{11} \text{ s}^{-1}$ . Calculate the ratio of the number of oscillators in the 10<sup>th</sup> quantum state ( $n=9$ ) to those in the ground state at 0 K, 300 K and 1000 K. The energy levels are given by  $\varepsilon_n = (n + \frac{1}{2})h\nu$ .

(This is a straight application of the Boltzmann distribution. Each energy level is non-degenerate.)

**Solution:**

Given:  $\nu = 10^{11} \text{ s}^{-1}$ ,  $n = 9$ ,  $T = 0 \text{ K}, 300 \text{ K}, 1000 \text{ K}$ ,  $\varepsilon_n = (n + \frac{1}{2})h\nu$

Required: ratio of the number of oscillators

$$\begin{aligned} \frac{N_{10}}{N_0} &= \frac{\exp(-\beta\varepsilon_9)}{\exp(-\beta\varepsilon_0)} = \frac{\exp\left(-\beta\left(9 + \frac{1}{2}\right)h\nu\right)}{\exp\left(-\beta\left(\frac{1}{2}\right)h\nu\right)} = \exp(-\beta 9h\nu) \\ &= \exp\left(-\frac{9h\nu}{k_B T}\right) = \exp\left(-\frac{9(6.623 \times 10^{-34} \text{ J s})(10^{11} \text{ s}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})T}\right) \\ &= \exp\left(-\frac{9(6.623 \times 10^{-34} \text{ J s})(10^{11} \text{ s}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})T}\right) = \exp\left(-\frac{3.8874 \times 10^2 \text{ K}^{-1}}{T}\right) \end{aligned}$$



$$\frac{N_{10}(T)}{N_0} = \exp\left(-\frac{3.8874 \times 10^2 \text{ K}^{-1}}{T}\right)$$

$$\frac{N_{10}(0)}{N_0} = \exp\left(-\frac{3.8874 \times 10^2 \text{ K}^{-1}}{0}\right)$$

$$\boxed{\frac{N_{10}(0)}{N_0} = 0}$$

$$\frac{N_{10}(300)}{N_0} = \exp\left(-\frac{3.8874 \times 10^2 \text{ K}^{-1}}{300}\right) = \exp(-1.129)$$

$$\boxed{\frac{N_{10}(300)}{N_0} = 0.274}$$

$$\frac{N_{10}(1000)}{N_0} = \exp\left(-\frac{3.8874 \times 10^2 \text{ K}^{-1}}{1000}\right) = \exp(-0.38874)$$

$$\boxed{\frac{N_{10}(1000)}{N_0} = 0.678}$$

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**15.27.** Calculate the average value of the energy per mole at the various temperatures for the oscillators in problem 17.

(This is best done by evaluating the partition function for harmonic oscillators and applying the general formula for  $\langle \varepsilon \rangle$ ).

**Solution:**

Given: problem 17

Required: average value of the energy per mole

You need to know the following sum:

$$\sum_{n=0}^{\infty} \exp(-xn) = \frac{1}{(1 - \exp(-x))}$$

Now calculate the partition function for the case that the energy is:  $\varepsilon_n = (n + \frac{1}{2})h\nu$

$$q = \sum_i \exp[-(\varepsilon_i - \varepsilon_0)/(k_B T)] = \sum_n \exp[-nh\nu\beta]$$

so

$$q = \frac{1}{(1 - \exp(-h\nu\beta))}$$

Now use:

$$\langle \varepsilon \rangle - \varepsilon_0 = -\frac{1}{q} \frac{dq}{d\beta} = -\frac{d \ln q}{d\beta}$$

$$\frac{1}{q} \frac{dq}{d\beta} = \frac{1}{q} \frac{d}{d\beta} \left( \frac{1}{(1 - \exp(-h\nu\beta))} \right) = \frac{1}{q} \left( -h\nu \frac{\exp(-h\nu\beta)}{(1 - \exp(-h\nu\beta))^2} \right)$$

$$\cancel{\frac{1}{q}} \left( \cancel{\frac{1}{(1 - \exp(-h\nu\beta))}} \right) \left( -h\nu \frac{\exp(-h\nu\beta)}{(1 - \exp(-h\nu\beta))} \right) = -\frac{h\nu}{(1 - \exp(h\nu\beta))}$$

so

$$\langle \varepsilon \rangle - \varepsilon_o = -\frac{1}{q} \frac{dq}{d\beta} = \frac{h\nu}{(\exp(h\nu\beta) - 1)}$$

or

$$\langle \varepsilon \rangle = \frac{h\nu}{2} + \frac{h\nu}{((\exp(h\nu\beta) - 1))}$$

$$\begin{aligned}\langle \varepsilon \rangle(T) &\rightarrow \langle \varepsilon \rangle(0) = \frac{h\nu}{2} + \frac{h\nu}{(\exp(\infty)-1)} = \frac{h\nu}{2} + \frac{h\nu}{\infty} \\ &= \frac{6.623 \times 10^{-23}}{2} = \boxed{3.31 \times 10^{-23} \text{ J molecule}^{-1} \text{ (zero point energy)}}\end{aligned}$$

$$\begin{aligned}\langle \varepsilon \rangle(300) &= \frac{h\nu}{2} + \frac{h\nu}{((\exp(h\nu\beta)-1))} = \frac{h\nu}{2} + \frac{6.623 \times 10^{-23} \text{ J molecule}^{-1}}{(\exp(6.623 \times 10^{-23} \text{ J} / (1.38 \times 10^{-23} \text{ J K}^{-1} \cdot 300 \text{ K})) - 1)} \\ &= \frac{h\nu}{2} + \frac{6.623 \times 10^{-23} \text{ J molecule}^{-1}}{(1.0161-1)} = \frac{h\nu}{2} + \frac{6.623 \times 10^{-23} \text{ J molecule}^{-1}}{0.0161} \\ &= \boxed{(0.0331 \times 10^{-21} + 4.173 \times 10^{-21}) = 4.206 \times 10^{-21} \text{ J molecule}^{-1}}\end{aligned}$$

$$\begin{aligned}\langle \varepsilon \rangle(1000) &= \frac{h\nu}{2} + \frac{h\nu}{((\exp(h\nu\beta)-1))} = \frac{h\nu}{2} + \frac{6.623 \times 10^{-23} \text{ J molecule}^{-1}}{(\exp(6.623 \times 10^{-23} \text{ J} / (1.38 \times 10^{-23} \text{ J K}^{-1} \cdot 1000 \text{ K})) - 1)} \\ &= \frac{h\nu}{2} + \frac{6.623 \times 10^{-23} \text{ J molecule}^{-1}}{(1.0048-1)} = \frac{h\nu}{2} + \frac{6.623 \times 10^{-23} \text{ J molecule}^{-1}}{0.0048} \\ &= \boxed{(0.00331 \times 10^{-20} + 1.3798 \times 10^{-20}) = 1.383 \times 10^{-20} \text{ J molecule}^{-1}}\end{aligned}$$

$$E = N \langle \varepsilon \rangle$$

$$\langle E \rangle(0) = 19.5 \text{ J mol}^{-1}$$

$$\langle E \rangle(300) = 2.533 \text{ kJ mol}^{-1}$$

$$\langle E \rangle(1000) = 8.329 \text{ kJ mol}^{-1}$$

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**15.28.** The energy levels for a harmonic oscillator are given by  $\varepsilon_n = \left( n + \frac{1}{2} \right) h\nu$ .

**a.** Derive an expression for the mean-square fluctuation,  $\sigma_E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2}$  in energy for these oscillators.

**b.** Use  $\nu = 10^{11} \text{ s}^{-1}$  and the partition function from problem set 2 to evaluate the mean-square fluctuation.

**c.** Compare  $\sigma_E$  to  $U = \langle E \rangle$ .

**d.** What happens as the temperature is raised?

**e.** What happens as the number of particles increases?

(Fluctuations are generally negligible relative to macroscopic quantities but are important for many processes under certain conditions, such as phase transitions.)

**Solution:**

Given:  $\varepsilon_n = \left( n + \frac{1}{2} \right) h\nu$

Required: see above

**a.**  $\langle E \rangle = \frac{\sum_j E_j \exp\left(-\frac{E_j}{k_B T}\right)}{q}$

or

$$\langle E \rangle \sum_j \exp\left(-\frac{E_j}{k_B T}\right) = \sum_j E_j \exp\left(-\frac{E_j}{k_B T}\right)$$

Differentiate with respect to  $T$ ,

$$\left(\frac{\partial E}{\partial T}\right)_{V,N} + \frac{\langle E \rangle}{Qk_B T^2} \sum_j E_j \exp\left(-\frac{E_j}{k_B T}\right) = \sum_j E_j^2 \exp\left(-\frac{E_j}{k_B T}\right)$$

or

$$\langle E^2 \rangle - \langle E \rangle^2 = \langle E - \langle E \rangle \rangle^2 = \sigma_E^2 = k_B T^2 C_V$$

$$\sigma_E = \sqrt{k_B T^2 C_V}$$

so the ratio of energy fluctuation to the average energy is

$$\frac{\sigma_E}{\langle E \rangle} = \frac{(k_B T^2 C_V)^{1/2}}{\langle E \rangle}$$

**b.** From Eq.(15.128)

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{Nk_B}{T^2} \left( \frac{\partial^2 \ln q}{\partial (1/T)^2} \right)_V$$

therefore

$$\sigma_E = \sqrt{k_B T^2 C_V} = \sqrt{\frac{Nk_B^2 T^2}{T^2} \left( \frac{\partial^2 \ln q}{\partial (1/T)^2} \right)_V} = k_B \sqrt{N \left( \frac{\partial^2 \ln q}{\partial (1/T)^2} \right)_V}$$

From Eq.(15.155), we have

$$q = \frac{1}{(1 - \exp(-h\nu\beta))}$$

Differentiating twice wrt  $1/T$ ,

$$\left( \frac{\partial^2 \ln q}{\partial (1/T)^2} \right)_V = \left( \frac{h\nu}{k_B} \right)^2 \frac{\exp\left(-\frac{h\nu}{k_B T}\right)}{\left(1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right)^3}$$

this gives

$$\sigma_E = \sqrt{k_B T^2 C_V} = k_B \sqrt{N \left( \frac{\partial^2 \ln q}{\partial (1/T)^2} \right)_V} = h\nu \sqrt{N} \frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{\left(1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right)^{3/2}}$$

or in numbers:

$$\sigma_E = h\nu \sqrt{N} \frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{\left(1 - \exp\left(-\frac{3h\nu}{2k_B T}\right)\right)} = 6.623 \times 10^{-23} \text{ J} \sqrt{N} \frac{\exp(-2.4/T)}{(1 - \exp(-4.799/T))^{3/2}}$$

c. We can calculate the average energy,

$$\langle \varepsilon \rangle = \frac{h\nu}{2} + \frac{h\nu}{((\exp(h\nu\beta) - 1))} \rightarrow \langle E \rangle = N \langle \varepsilon \rangle = \frac{Nh\nu}{2} + \frac{Nh\nu}{((\exp(h\nu\beta) - 1))}$$

giving

$$\langle E \rangle = \frac{Nh\nu}{2} + \frac{(6.023 \times 10^{23} \text{ molecule})(6.623 \times 10^{-23} \text{ J molecule}^{-1})}{\left(\exp(6.623 \times 10^{-23} \text{ J} / (1.38 \times 10^{-23} \text{ J K}^{-1} \cdot T \text{ K})) - 1\right)}$$

$$\langle E \rangle = n \left( 19.9 \text{ J} + \frac{39.9 \text{ J}}{\exp(4.799/T) - 1} \right)$$

where  $n$  is the number of moles. Therefore the ratio is

$$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{N}}{n} \left[ \frac{6.623 \times 10^{-23} \text{ J} \frac{\exp(-2.4/T)}{(1 - \exp(-4.799/T))^{3/2}}}{\left( 19.9 \text{ J} + \frac{39.9 \text{ J}}{\exp(4.799/T) - 1} \right)} \right]$$

which shows that the fluctuations are very small.

- d. Clearly at  $T=0 \text{ K}$  the exponentials in the numerator vanish, while the denominator shows the second term vanishes. As  $T$  increases, these terms become important. If you want to expand the exponentials in  $1/T$ , then you will see what happens at high temperature, but that is not necessary for the problem.
- e. From the above equation,

$$\sigma_E = \sqrt{k_B T^2 C_V} = \sigma_E = h\nu \sqrt{N} \frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{\left(1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right)^{3/2}}$$

It is clear that the fluctuations increase as the square root of  $N$ . Parts d. and show us that fluctuations increase with temperature and density.

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**15.29.** If the molecular partition function can be written as a product of factors,  $q = q_{tr} \cdot q_{int}$ , then energy, entropy and the other thermodynamic properties can be written as a sum of terms. Show that this is true for  $E$ ,  $S$  and  $A$ .

**Solution:**

Given:  $q = q_{tr} \cdot q_{int}$

Required: show that  $E$ ,  $S$ , and  $A$  can be written as a sum of terms

$$E - E_o = RT^2 \left( \frac{\partial \ln q}{\partial T} \right)_V = RT^2 \left( \frac{\partial \ln (q_1 q_2)}{\partial T} \right)_V$$

$$E - E_o = RT^2 \left[ \left( \frac{\partial \ln q_1}{\partial T} \right)_V + \left( \frac{\partial \ln q_2}{\partial T} \right)_V \right] = E_1 + E_2 - E_{1o} - E_{2o}$$

For the entropy and the Hemholtz energy you have to decide where the factorial goes. Therefore we write  $q = q_{tr} q_{int}$

$$\begin{aligned} S &= Nk_B \left[ \ln q_{tr} q_{int} - \ln N + 1 - \left( \frac{\partial \ln q_{tr} q_{int}}{\partial \ln T} \right)_V \right] \\ &= Nk_B \left[ \ln \frac{q_{tr}}{N} q_{int} + 1 - \left( \frac{\partial \ln q_{tr}}{\partial \ln T} \right)_V - \left( \frac{\partial \ln q_{int}}{\partial \ln T} \right)_V \right] \\ &= Nk_B \left[ \ln \frac{q_{tr}}{N} + 1 - \left( \frac{\partial \ln q_{tr}}{\partial \ln T} \right)_V \right] - Nk_B \left[ \ln q_{int} - \left( \frac{\partial \ln q_{int}}{\partial \ln T} \right)_V \right] \\ &= Nk_B \left[ \ln \frac{q_{tr}}{N} - \ln N + 1 - \left( \frac{\partial \ln q_{tr}}{\partial \ln T} \right)_V \right] - Nk_B \left[ \ln q_{int} - \left( \frac{\partial \ln q_{int}}{\partial \ln T} \right)_V \right] \\ &= S_{tr} + S_{int} \\ A &= -Nk_B T \left[ \ln \frac{q}{N} + 1 \right] = -Nk_B T \left[ \ln \frac{q_{tr}}{N} + 1 \right] - Nk_B T \ln q_{int} \\ &= A_{tr} + A_{int} \end{aligned}$$

From here on, you can put in the  $q_{\text{int}}$  as a product and the energies, entropy and free energies become a sum.

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**15.30.** Calculate  $\frac{h^2}{8ma^2}$  for helium in a one-dimensional box of  $a=10$  cm and determine the energy level spacing for the first four levels.

Compare this with  $k_B T$ . At what temperature are the energy levels spacing comparable in magnitude?

**Solution:**

Given:  $a=10$  cm

Required: value of  $\frac{h^2}{8ma^2}$ , energy level spacing, compare energy level spacing with  $k_B T$ , temperature at which the energy levels spacing are comparable

$$\frac{h^2}{8ma^2} = \frac{(6.626 \times 10^{-34} \text{ J-s})^2}{8 \times 4 \times 1.673 \times 10^{-27} \text{ kg} \times (0.1)^2 \text{ m}^2}$$

$$\boxed{\frac{h^2}{8ma^2} = 8.2 \times 10^{-40} \text{ J}}$$

Energy levels:  $\frac{n^2 h^2}{8ma^2}$

n	energy (J)	difference(J)	degrees K
1	$8.2 \times 10^{-40}$		
		$24.6 \times 10^{-40}$	$1.8 \times 10^{-16}$
2	$32.8 \times 10^{-40}$		
		$41 \times 10^{-40}$	$3 \times 10^{-16}$
3	$73.8 \times 10^{-40}$		
		$57 \times 10^{-40}$	$4 \times 10^{-16}$
4	$131. \times 10^{-40}$		

The thermal energy is  $k_B T$ , and the energy splitting for the translational energy is of the order of  $10^{-16}$  K. That is, only at temperatures below about  $10^{-16}$  K are these states not in the high temperature approximation. Therefore at any reasonable temperature, the translation energy levels are all occupied and are in the classical limit (high  $T$ ).

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**15.31.** Calculate  $\Theta_v$  for  $\text{H}_2$  (frequency =  $4162 \text{ cm}^{-1}$ ) and  $\text{I}_2$  (frequency =  $213.1 \text{ cm}^{-1}$ ). Calculate  $q_v$  for these gases at 300 K.

**Solution:**

Given: for  $\text{H}_2$  : frequency =  $4162 \text{ cm}^{-1}$ , for  $\text{I}_2$  : frequency =  $213.1 \text{ cm}^{-1}$ ,  $T = 300 \text{ K}$

Required:  $\Theta_v$ ,  $q_v$

$$q_v = \frac{1}{1 - \exp\left(-\frac{\Theta_v}{T}\right)}$$

For  $\text{H}_2$ ,

$$\Theta_v = \frac{h\nu}{k_B} = \frac{(6.626 \times 10^{-34} \text{ J-s})(4162 \text{ cm}^{-1})(3 \times 10^{10} \text{ cm s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1})}$$

$$\boxed{\Theta_v = 5990 \text{ K}}$$

$$q_v = \frac{1}{1 - \exp\left(-\frac{5990}{300}\right)} = \frac{1}{1 - 0.9998293} = 5859$$

For  $\text{I}_2$ ,

$$\Theta_v = \frac{h\nu}{k_B} = \frac{(6.626 \times 10^{-34} \text{ J-s})(213.1 \text{ cm}^{-1})(3 \times 10^{10} \text{ cm s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1})} = 306.7 \text{ K}$$

$$q_v = \frac{1}{1 - \exp\left(-\frac{306.7}{300}\right)} = 1.562$$

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**15.32.** Starting with the molecular partition function, prove for diatomic molecules in the high temperature limit that the translational, rotational and vibrational contributions to the heat capacity agree with the expression from equipartition.

**Solution:**

Given: see above

Required: see above

This is for diatomics.

$$E_{tr} - E_o = Lk_B T^2 \left( \frac{\partial \ln q_{tr}}{\partial T} \right)_v = \frac{Lk_B T^2}{q} \left( \frac{\partial q_{tr}}{\partial T} \right)_v$$

$$E_{tr} - E_o = \frac{Lk_B T^2}{q} \left( \frac{2\pi mk_B}{h^2} \right)^{3/2} \frac{3}{2} T^{1/2} = \frac{Lk_B T^2}{\left( \frac{2\pi mk_B T}{h^2} \right)^{3/2}} \left( \frac{2\pi mk_B}{h^2} \right)^{3/2} \frac{3}{2} T^{1/2}$$

$$E_{tr} - E_o = \frac{Lk_B T^2}{T^{3/2}} \frac{3}{2} T^{1/2} = \frac{Lk_B T^2}{T} \frac{3}{2} = \frac{3}{2} Lk_B T = \frac{3}{2} RT$$

Rotation:  $q_r = \frac{T}{\sigma \Theta_r}$

$$E_r - E_o = \frac{Lk_B T^2}{q_r} \left( \frac{\partial q_r}{\partial T} \right)_v = \frac{Lk_B T^2}{\left( \frac{T}{\sigma \Theta_r} \right)} \frac{1}{\cancel{\sigma \Theta_r}} \left( \frac{\partial T}{\partial T} \right)_v$$

$$E_r - E_o = \frac{Lk_B T^2}{T} = Lk_B T = RT$$

Vibration:  $q_v = \frac{T}{\Theta_v}$

$$E_v - E_o = \frac{Lk_B T^2}{q_r} \left( \frac{\partial q_v}{\partial T} \right)_v = \frac{Lk_B T^2}{\left( \frac{T}{\cancel{\phi_r}} \right) \cancel{\phi_r}} \left( \frac{\partial T}{\partial T} \right)_v$$

$$E_v - E_o = \frac{Lk_B T^2}{T} = Lk_B T = RT$$

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**15.33.** Work out the heat capacity,  $C_v$ , at 300 K for the diatomic molecules listed below. Keep only the translational, rotational and vibrational motion. Use table below for the rotational and vibrational temperatures. Only use the high temperature approximation if it is valid. HCl, N<sub>2</sub>, O<sub>2</sub>, I<sub>2</sub>

	$q_{tr}$	$q_r$	$q_v$
HCl	High temp.	19.73	1.0000016
N <sub>2</sub>	High temp.	104.89	1.0000146
O <sub>2</sub>	High temp.	144.92	1.00059
I <sub>2</sub>	High temp.	555.5	1.552

**Solution:**

Given:  $T = 300$  K, above table

Required:  $C_v$

	$\square$ K	$\square$ K	$r_e$ Å	$D_0$ eV
HCl	4140	15.2	1.275	4.43
N <sub>2</sub>	3340	2.86	1.095	9.76
O <sub>2</sub>	2230	2.07	1.204	5.08
I <sub>2</sub>	310	0.054	2.667	1.54

Translational:



$$q_t = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V = \frac{V}{\Lambda^3} \quad \text{From question 1, these are all high temperature so we can take the contribution to the heat capacity as}$$

$$\frac{3}{2}R$$

Rotational:

$$q_r = \sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{j(j+1)\Theta_r}{T}\right) \quad \text{where } \Theta_r = \frac{h^2}{8\pi^2 k_B I}$$

or at high temperatures:

$$q_r = \frac{T}{\sigma \Theta_r}$$

If we look at the table, we can see that the largest rotational temperature is 15.2 K. Hence only for HCl might we have a deviation from the high temperature approximation. So for HCl we have:

$$q_r = \sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{j(j+1) \times 15.2}{300}\right) = 1 + 3 \exp\left(-\frac{2 \times 15.2}{300}\right) + 5 \exp\left(-\frac{6 \times 15.2}{300}\right) \dots$$

$$= 1 + \underbrace{2.7109}_{j=1} + \underbrace{3.6893}_{j=2} + \underbrace{3.8110}_{j=3} + \underbrace{3.2671}_{j=4} + \underbrace{2.4058}_{j=5} + \underbrace{1.5480}_{j=6} + \underbrace{0.8787}_{j=7} + \underbrace{0.4427}_{j=8} + \underbrace{0.1987}_{j=9} + \underbrace{0.079}_{j=10} \dots$$

$$= 20.03$$

If we compare this with the high temperature limit, we get:

$$q_r = \frac{T}{\Theta_r} = \frac{300}{15.2} = 19.73 \quad \text{Therefore for the rotational motion, HCl is in the high temperature limit at 300 K. Hence all the others are in the high temperature limit too.}$$

Vibrational:

$q_v = \left(1 - \exp\left(-\frac{\Theta_v}{T}\right)\right)^{-1}$  We can just plug in the values and calculate the result (see next table):

$q_v = \left(1 - \exp\left(-\frac{4140}{300}\right)\right)^{-1} = 1.0000016$  etc. (see table) Clearly all but  $I_2$  are close to “1” meaning that the vibrational contributions are not in the high temperature approximation.

To calculate the heat capacity for each, the contribution from translational and rotational is the same, being the high temperature approximation:

$$C_v = \underbrace{\frac{3}{2}R}_{\text{translational}} + \underbrace{R}_{\text{Rotational}} = \frac{5}{2}R \text{ which is good for HCl, N}_2 \text{ and O}_2. \text{ For I}_2, \text{ we have to do a bit more work:}$$

From Eq.(9.38):

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{Lk_B}{T^2} \left( \frac{\partial^2 \ln q}{\partial \left(\frac{1}{T}\right)^2} \right)_v = \frac{Lk_B}{T^2} \left( \frac{\partial^2 \ln q}{\partial x^2} \right)_v \text{ where } x = T^{-1}.$$

This is the calculation for the contribution from vibration to the heat capacity of  $I_2$ .

$$\begin{aligned}
C_V &= \frac{Lk_B}{T^2} \left( \frac{\partial^2 \ln q_v}{\partial x^2} \right)_v = \frac{Lk_B}{T^2} \frac{\partial}{\partial x} \left( \frac{\partial \ln q_v}{\partial x} \right)_v = \frac{Lk_B}{T^2} \frac{\partial}{\partial x} \frac{1}{q_v} \left( \frac{\partial q_v}{\partial x} \right)_v \\
&= \frac{Lk_B}{T^2} \frac{\partial}{\partial x} \frac{1}{q_v} \left( \frac{\partial}{\partial x} \left[ \frac{1}{1 - e^{-\Theta_v/x}} \right] \right) = \frac{Lk_B}{T^2} \frac{\partial}{\partial x} \frac{1}{q_v} \left( \frac{-\Theta_v e^{-\Theta_v/x}}{(1 - e^{-\Theta_v/x})^2} \right) \\
&= \frac{Lk_B}{T^2} \frac{\partial}{\partial x} \left( \frac{-\Theta_v e^{-\Theta_v/x}}{(1 - e^{-\Theta_v/x})} \right) = -\frac{Lk_B \Theta_v}{T^2} \frac{\partial}{\partial x} \left( \frac{1}{(e^{\Theta_v/x} - 1)} \right) = -\frac{Lk_B \Theta_v}{T^2} \left( \frac{-\Theta_v e^{\Theta_v/x}}{(e^{\Theta_v/x} - 1)^2} \right) \\
&= \frac{Lk_B \Theta_v^2}{T^2} \left( \frac{e^{\Theta_v/x}}{(e^{\Theta_v/x} - 1)^2} \right) = \frac{Lk_B (310)^2}{(300)^2} \left( \frac{e^{310/300}}{(e^{310/300} - 1)^2} \right) = 0.8524R
\end{aligned}$$

Hence the heat capacity of  $I_2$  is  $C_V = \frac{5}{2}R + 0.8524R = 3.3524R = 27.87 \text{ J K}^{-1} \text{ Mol}^{-1}$

Experimentally, the heat capacities of HCl,  $N_2$ , and  $O_2$  are very close to  $2.5R$ . This shows that at 300 K the calculations are correct if the vibrational contributions are ignored. In contrast for Iodine, has contributions from the vibrational parts. Unfortunately it is a solid at 300 K and does not boil until over 400 K, so we do not have data at 300 K. On the other hand, above the boiling point you can see that the heat capacity of iodine will be  $3.5R$ , since the vibrational contributions will then be in high temperature limit.

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**15.34.** The high temperature limit of the rotational partition function for diatomics is

$$q_r = \frac{T}{\sigma \Theta_r}$$

Give a brief explanation of the quantum mechanical origin of the symmetry number  $\sigma$ . Use equations where appropriate.

**Solution:**

Given:  $q_r = \frac{T}{\sigma \Theta_r}$

Required: explanation

Symmetry restrictions due to permutation symmetry lead to the sum over rotational states omitting certain values. For homonuclear diatomics, one half of the states are missing. For example,  $\text{O}_2^{16}$  (Hill page 469) has a rotational partition function of,

$$q_{rn} = \sum_{j=\text{even}} \dots \xrightarrow{\text{high temperature}} \frac{1}{2} \sum_{\text{all } j \text{ values}} \dots$$

This explains the quantum mechanical origin of the symmetry number = 2.

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**15.35.** Prove that the Einstein function for the vibrational contribution to the heat capacity, Eq.(15.183) can be written as,

$$(C_V)_{\text{Einstein}} = R \left( \frac{u}{2} \coth \frac{u}{2} \right)^2$$

where

$$u = \frac{h\nu}{k_B T} = \frac{\Theta_v}{T}.$$

Show that the limiting value of Einstein function, Eq.(15.183), is the gas constant,  $R$ . (Recall that the Einstein vibration is restricted to one frequency only so this is consistent with equipartition that states at high temperatures the contribution to the heat capacity is equal to  $R$  for each degree of freedom. In this case, there is only one degree of freedom.)

**Solution:**

Given: see above

Required: see above

The vibrational contribution to the heat capacity, Eq.(15.166)

$$C_V = R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{[e^{\Theta_E/T} - 1]^2}$$

$$C_V = R \frac{u^2 e^u}{[e^u - 1]^2} = R \frac{u^2}{[e^{u/2} - e^{-u/2}]^2}$$

where  $u = \Theta_E/T$ . Using  $\text{cosech } u = \frac{1}{\sinh u} = \frac{2}{e^u - e^{-u}}$  gives,

$$C_V = R \frac{u^2}{4} \frac{4}{[e^{u/2} - e^{-u/2}]^2} = R \left( \frac{u}{2} \text{cosech } \frac{u}{2} \right)^2$$

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**15.36.** Starting with Eq. (15.156) obtain an expression for the molar internal energy  $U_m$  of an ideal monatomic gas.

**Solution:**

Given: Eq. 15.156

Required: obtain expression for  $U_m$

Einstein's expression is:

$$(\tilde{C}_V)_{Einstein} = R \frac{u^2 \exp(u)}{(\exp(u) - 1)^2}$$

where  $u = \frac{h\nu_E}{k_B T} = \frac{\Theta_E}{T}$  so as  $T \rightarrow \infty$ ,  $u \rightarrow 0$ , and  $\exp(u) \rightarrow 1$  except for the denominator,

$$(\tilde{C}_V)_{Einstein} = R \frac{u^2 \exp(u)}{(\exp(u) - 1)^2} \xrightarrow{T \rightarrow \infty} R \frac{u^2}{(1 + u - 1)^2} = R$$

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**15.37.** Calculate the molecular translational partition functions  $q_t$  for (a)  $\text{N}_2$ , (b)  $\text{H}_2\text{O}$ , (c)  $\text{C}_6\text{H}_6$  in a volume of  $1 \text{ m}^3$  at 300 K. In each case, calculate also  $\ln Q_{t,m}$ , where  $Q_{t,m}$  is the molar translational partition function.

**Solution:**

Given:  $V = 1 \text{ m}^3$ ,  $T = 300 \text{ K}$

Required: molar translational partition functions,  $\ln Q_{t,m}$

From Eq. 15.86, we know that

$$q_t = \frac{(2\pi mk_{\text{B}}T)^{3/2} V}{h^3}$$
$$q_t = \frac{(2\pi \times 1.381 \times 10^{-23} \times 300)^{3/2}}{(6.626 \times 10^{-34})^3} (\text{m/kg})^{3/2}$$
$$\boxed{q_t = 1.444 \times 10^{70} (\text{m/kg})^{3/2}}$$

a. For  $N_2$ :

$$m = \frac{2 \times 14.0067 \cancel{\text{g}} \cancel{\text{mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{g}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}}$$

$$m = 4.651\,843\,241 \times 10^{-26} \text{ kg}$$

$$q_t = \frac{(2\pi \times 1.381 \times 10^{-23} \times 300 \times 4.651\,843\,241 \times 10^{-26})^{3/2}}{(6.626 \times 10^{-34})^3}$$

$$\boxed{q_t = 1.449 \times 10^{32}}$$

For  $N$  indistinguishable molecules,

$$\ln Q = N \ln q - N \ln N + N$$

$$\text{Here } N = 6.022 \times 10^{23}$$

$$\ln Q_{t,m} = 6.022 \times 10^{23} \times \ln(1.449 \times 10^{32}) - 6.022 \times 10^{23} \times \ln(6.022 \times 10^{23}) + 6.022 \times 10^{23}$$

$$\ln Q_{t,m} = 1.222\,388\,923 \times 10^{25}$$

$$\boxed{\ln Q_{t,m} = 1.223 \times 10^{25}}$$

b. For  $H_2O$ :

$$m = \frac{18.015 \cancel{\text{g}} \cancel{\text{mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{g}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}}$$



$$m = 2.991\,531\,053 \times 10^{-26} \text{ kg}$$

$$q_t = \frac{(2\pi \times 1.381 \times 10^{-23} \times 300 \times 2.991\,531\,053 \times 10^{-26})^{3/2}}{(6.626 \times 10^{-34})^3}$$

$$\boxed{q_t = 7.47 \times 10^{31}}$$

$$\ln Q_{t,m} = 6.022 \times 10^{23} \times \ln(7.47 \times 10^{31}) - 6.022 \times 10^{23} \times \ln(6.022 \times 10^{23}) + 6.022 \times 10^{23}$$

$$\ln Q_{t,m} = 1.182\,489\,333 \times 10^{25}$$

$$\boxed{\ln Q_{t,m} = 1.182 \times 10^{25}}$$

c. For  $\text{C}_6\text{H}_6$ :

$$m = \frac{78.114 \text{ g mol}^{-1} \times 10^{-3} \text{ kg g}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$m = 1.297\,143\,806 \times 10^{-25} \text{ kg}$$

$$q_t = \frac{(2\pi \times 1.381 \times 10^{-23} \times 300 \times 1.297\,143\,806 \times 10^{-25})^{3/2}}{(6.626 \times 10^{-34})^3}$$

$$\boxed{q_t = 6.746 \times 10^{32}}$$

$$\ln Q_{t,m} = 6.022 \times 10^{23} \times \ln(6.746 \times 10^{32}) - 6.022 \times 10^{23} \times \ln(6.022 \times 10^{23}) + 6.022 \times 10^{23}$$

$$\ln Q_{t,m} = 1.315\,011\,864 \times 10^{25}$$

$$\boxed{\ln Q_{t,m} = 1.315 \times 10^{25}}$$

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**15.38.** The internuclear distance for  $\text{N}_2$  is 0.1095 nm. Determine the molecular rotational partition function  $q_r$  and  $\ln Q$  for  $\text{N}_2$  at 300 K.

**Solution:**

Given:  $d = 0.1095$  nm,  $T = 300$  K

Required:  $q_r$ ,  $\ln Q$

$$\text{Mass of N atom} = \frac{14.0067 \cancel{\text{g}} \cancel{\text{mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{g}^{-1}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}}$$

$$\text{Mass of N atom} = 2.325\,921\,621 \times 10^{-26} \text{ kg}$$

Moment of inertia of  $\text{N}_2$

$$I = \frac{1}{2} \times 2.325\,921\,621 \times 10^{-26} \times (0.1095 \times 10^{-9})^2$$

$$I = 1.394\,419\,086 \times 10^{-46} \text{ kg m}^2$$

The symmetry number is 2.

$$q_r = \frac{8\pi^2 (1.394\,419\,086 \times 10^{-46}) (1.381 \times 10^{-23}) (300)}{2 (6.626 \times 10^{-34})^2}$$

$$q_r = 51.947\,556\,65$$

$$\boxed{q_r = 51.9}$$

$$\ln Q_r = L \ln q_r$$

$$\ln Q_r = (6.022 \times 10^{23}) \ln (51.947\,556\,65)$$

$$\ln Q_r = 2.378\,831\,327 \times 10^{24}$$

$$\boxed{\ln Q_r = 2.38 \times 10^{24}}$$

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**15.39.** Use the data in Table 15.3 (p. 807) to calculate, with reference to  $v = 0$ , the molecular vibrational partition function for  $\text{CO}_2$  at (a) 300 K and (b) 3000 K.

**Solution:**

Given: Table 15.3,  $v = 0$

Required: molecular vibrational partition function for  $\text{CO}_2$

The molecular vibrational partition function is

$$q_v = \frac{1}{1 - \exp\left(\frac{-1890}{T}\right)} \times \frac{1}{1 - \exp\left(\frac{-3360}{T}\right)} \left( \frac{1}{1 - \exp\left(\frac{-954}{T}\right)} \right)^2$$

$$\text{a. } q_v = \frac{1}{1 - \exp\left(\frac{-1890}{300}\right)} \times \frac{1}{1 - \exp\left(\frac{-3360}{300}\right)} \left( \frac{1}{1 - \exp\left(\frac{-954}{300}\right)} \right)^2$$

$$q_v = 1.001\,839\,683 \times 1.000\,013\,674 \times 1.088\,662\,816$$

$$q_v = 1.090\,680\,524$$

$$\boxed{q_v = 1.09}$$

$$\text{b. } q_v = \frac{1}{1 - \exp\left(\frac{-1890}{3000}\right)} \times \frac{1}{1 - \exp\left(\frac{-3360}{3000}\right)} \left( \frac{1}{1 - \exp\left(\frac{-954}{3000}\right)} \right)^2$$

$$q_v = 2.139\,457\,549 \times 1.484\,295\,694 \times 13.477\,045\,2$$

$$q_v = 42.797\,537\,98$$

$$\boxed{q_v = 42.8}$$

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**15.40.** Expressions such as the Sackur-Tetrode equation for the entropy contain a term  $\ln(\text{constant} \times T)$ . At temperatures close to the absolute zero this term has large negative values, and the expression therefore leads to a negative value of the entropy. Comment on this.

**Solution:**

Given: see above

Required: comment on the observed phenomenon

The Sackur-Tetrode equation is based on Eq. 15.86 for the translational partition function. This expression was obtained by replacing a summation (Eq. 15.83) by an integration (Eq. 15.84), a procedure that is valid only if the spacing between the translation levels is much smaller than  $k_B T$ . This approximation is not valid at extremely low temperatures, and the Sackur-Tetrode equation then is inapplicable.

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**15.41.** Calculate the entropy of argon gas at 25 °C and 1 bar pressure.

**Solution:**

Given:  $T = 25\text{ °C}$ ,  $P = 1\text{ bar}$

Required: entropy

From the Sackur-Tetrode equation (Eq. 15.88),

$$S / \text{J K}^{-1} \text{ mol}^{-1} = 108.74 + 12.47 \ln M_r$$

For argon,  $M_r = 39.948$  and therefore,

$$S / \text{J K}^{-1} \text{ mol}^{-1} = 108.74 + 45.98 = 154.7$$

$$\boxed{S = 154.7 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**15.42.** From the data in Table 15.3, calculate, with reference to  $v = 0$ , the molecular vibrational partition function for  $\text{Br}_2$  at (a) 300 K and (b) 3000 K.

**Solution:**

Given: Table 15.3,  $v = 0$

Required: molecular vibrational partition function

The value of  $\theta_v$  is 470 K and thus,

$$q_v = \frac{1}{1 - \exp\left(\frac{-470 \text{ K}}{T}\right)}$$

**a.** At  $T = 300 \text{ K}$ ,

$$q_v = \frac{1}{1 - \exp\left(\frac{-470 \text{ K}}{300 \text{ K}}\right)}$$

$$q_v = 1.263 \ 806 \ 81$$

$$\boxed{q_v = 1.26}$$

**b.** At  $T = 3000 \text{ K}$ ,

$$q_v = \frac{1}{1 - \exp\left(\frac{-470 \text{ K}}{3000 \text{ K}}\right)}$$

$$q_v = 6.896 \ 028 \ 941$$

$$\boxed{q_v = 6.90}$$

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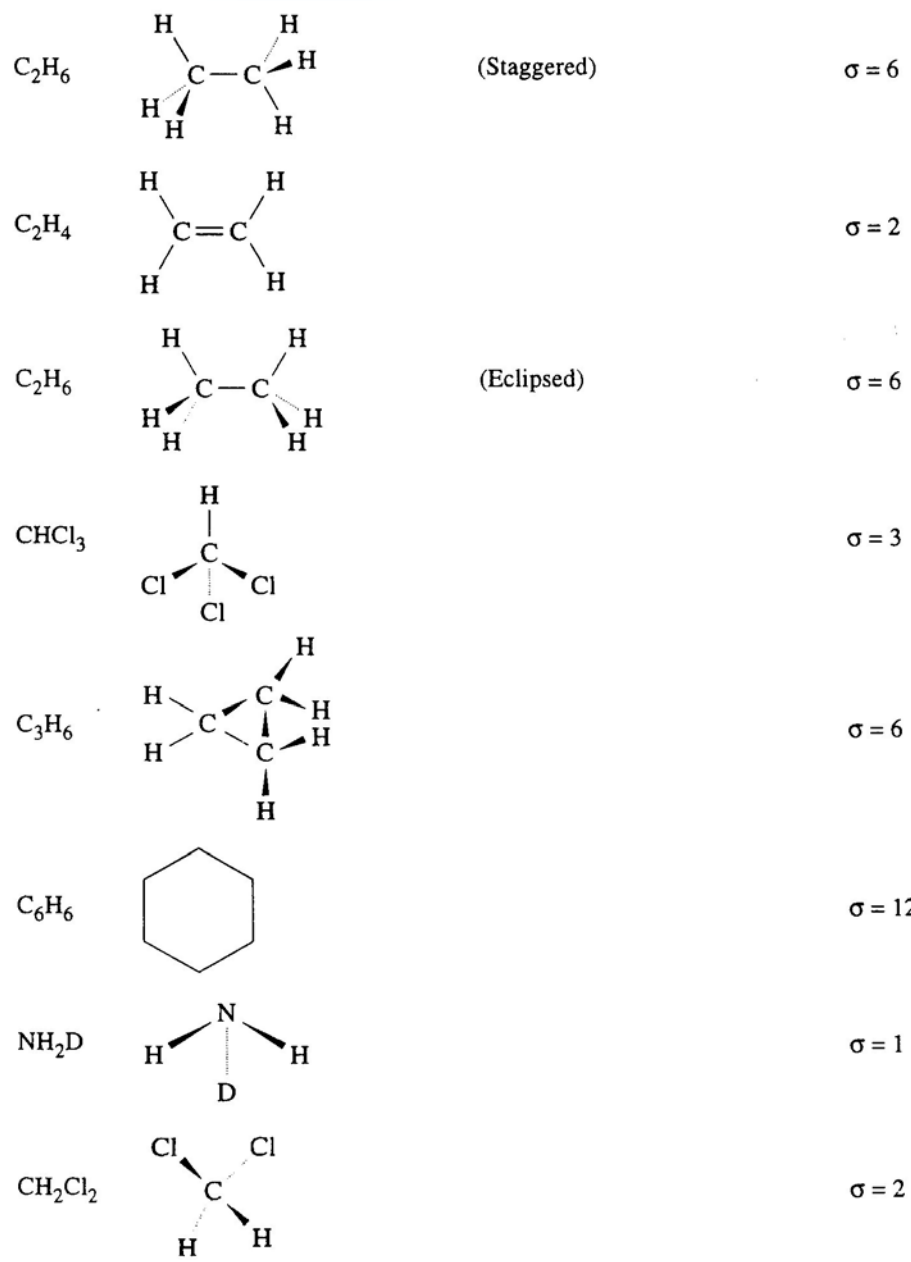
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**15.43.** Give the symmetry numbers of the following molecules:  $\text{C}_3\text{O}_2$  (carbon suboxide),  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  in the staggered conformation,  $\text{C}_2\text{H}_6$  in the eclipsed conformation,  $\text{CHCl}_3$ ,  $\text{C}_3\text{H}_6$  (cyclopropane),  $\text{C}_6\text{H}_6$  (benzene),  $\text{NH}_2\text{D}$ ,  $\text{CH}_2\text{Cl}_2$ .

**Solution:**

Given: see above

Required: symmetry numbers

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**15.44.** Show that the rotational partition function for a linear molecule can be expressed as

$$q_r = k_B T / \sigma B h$$

where  $B$  is the rotational constant defined by Eq.(13.63).

**Solution:**

Given: see above

Required: see above

The rotational constant is

$$B = \frac{h}{8\pi^2 I}$$

We know that

$$q_r = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

Therefore, we can substitute the expression for  $B$  into the above equation and yield:

$$q_r = \frac{k_B T}{\sigma B h}$$

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**\*15.45.** Calculate the molar translational entropy of chlorine gas at 25 °C and 0.1 bar pressure.

**Solution:**

Given:  $T = 25\text{ °C}$ ,  $P = 1\text{ bar}$

Required: molar translational entropy

We use Eq. 15.88 with  $V_m = \frac{Lk_B T}{P}$ :

$$S_m = \frac{5}{2}R + R \ln \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \right]$$

$$\text{For Cl}_2, m = \frac{2 \times 35.45 \cancel{\text{ g}} \cancel{\text{ mol}^{-1}} \times 10^{-3} \text{ kg} \cancel{\text{ g}}}{6.022 \times 10^{23} \cancel{\text{ mol}^{-1}}} 1.177\,349\,718 \times 10^{-25} \text{ kg}$$

$$P = 0.1 \text{ bar} = 1.00 \times 10^4 \text{ Pa}$$

Plug the values into the expression for  $S_m$ , we get:

$$S_m = \frac{5}{2} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \\ \times \ln \left[ \left( \frac{2\pi \times 1.177\,349\,718 \times 10^{-25}}{(6.626 \times 10^{-34})^2} \right)^{3/2} \frac{(1.381 \times 10^{-23} \times 298.15)}{1.00 \times 10^4} \right]$$

$$S_m = 20.786\,25 \text{ J K}^{-1} \text{ mol}^{-1} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \\ \times \ln(2.187\,125\,651 \times 10^{63} \times 4.117\,451\,5 \times 10^{-25})$$

$$S_m = 20.786\,25 \text{ J K}^{-1} \text{ mol}^{-1} + 745.777\,858\,7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_m = 766.564\,108\,7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{S_m = 766.6 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**\*15.46.** The carbon monoxide molecule has a moment of inertia of  $1.45 \times 10^{-46} \text{ kg m}^2$  and its vibrational frequency is  $6.50 \times 10^{13} \text{ s}^{-1}$ . Calculate the translational, rotational, and vibrational contributions to the molar entropy of carbon monoxide at  $25^\circ\text{C}$  and 1 bar pressure.

**Solution:**

Given:  $I = 1.45 \times 10^{-46} \text{ kg m}^2$ ,  $\nu = 6.50 \times 10^{13} \text{ s}^{-1}$ ,  $T = 25^\circ\text{C}$ ,  $P = 1 \text{ bar}$

Required: translational, rotational, and vibrational contributions to the molar entropy

The translational entropy is given by the Sackur-Tetrode equation (Eq. 15.90)

$$S_{t,m} / \text{J K}^{-1} \text{ mol}^{-1} = 108.74 + 12.47 \ln(M_r)$$

Here,  $M_r$  is the relative molecular mass of the compound

For carbon monoxide, the relative molecular mass is

$$M_r = 12.00 + 16.01 = 28.01 \text{ g mol}^{-1}$$

Therefore,

$$S_{t,m} / \text{J K}^{-1} \text{ mol}^{-1} = 108.74 + 12.47 \ln(28.01)$$

$$S_{t,m} = 150.297 \text{ 043 J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{S_{t,m} = 150.3 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The rotational partition function is

$$q_r = \frac{8\pi^2 I k_B T}{h^2}$$

$$q_r = \frac{8\pi^2 \times 1.45 \times 10^{-46} \cancel{\text{kg}} \cancel{\text{m}^2} \times 1.381 \times 10^{-23} \cancel{\text{m}^2} \cancel{\text{kg}} \cancel{\text{s}^{-2}} \cancel{\text{K}^{-1}} \times 298.15 \cancel{\text{K}}}{(6.626 \times 10^{-34})^2 \cancel{\text{m}^4} \cancel{\text{kg}^2} \cancel{\text{s}^{-2}}}$$

$$q_r = 107.370 \text{ 101 5}$$

The rotational entropy is

$$S_r = k_B T \left( \frac{\partial \ln Q_r}{\partial T} \right)_V + k_B \ln Q$$

$$S_{r,m} = RT \left( \frac{\partial \ln q_r}{\partial T} \right)_V + R \ln q_r \quad \text{since } Q_r = q_r^N$$

$$S_{r,m} = R + R \ln q_r$$

$$S_{r,m} / \text{J K}^{-1} \text{ mol}^{-1} = 8.3145 + 8.3145 \ln 107.370 \text{ } 101 \text{ } 5$$

$$S_{r,m} = 47.195 \text{ } 444 \text{ } 68 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{S_{r,m} = 47.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Since  $\nu = 6.50 \times 10^{13} \text{ s}^{-1}$ , the spacing between vibrational energy levels is

$$h\nu = 6.626 \times 10^{-34} \times 6.50 \times 10^{13} = 4.3069 \times 10^{-20} \text{ J}$$

$$\frac{h\nu}{k_B T} = \frac{4.3069 \times 10^{-20} \cancel{\text{J}}}{1.381 \times 10^{-23} \cancel{\text{m}^2 \text{kg s}^{-2} \text{K}^{-1}} \times 298.15 \cancel{\text{K}}}$$

$$\frac{h\nu}{k_B T} = 10.460 \text{ } 111 \text{ } 07$$

$$q_v = \frac{1}{1 - \exp(-10.460 \text{ } 111 \text{ } 07)} = 1.000 \text{ } 028 \text{ } 658$$

$$q_v \approx 1$$

The vibrational energy is therefore negligible.

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**15.47.** Suppose that a system has equally spaced energy levels, the separation between neighboring levels being  $\Delta\epsilon$ . Prove that the fraction of the molecules in state  $i$ , having energy  $\epsilon_i$  greater than the energy of the lowest level, is

$$1 - \exp\left(\frac{-\Delta\epsilon}{k_B T}\right) \exp\left(\frac{-\epsilon_i}{k_B T}\right)$$

What is the limiting value of this fraction as  $T \rightarrow \infty$ ? Explain your answer.

**Solution:**

Given: see above

Required: limiting value as  $T \rightarrow \infty$ , explanation

The fraction of molecules in the  $i$ -th level is

$$\begin{aligned} & \frac{\exp\left(\frac{-\epsilon_i}{k_B T}\right)}{1 + \exp\left(\frac{-\epsilon_1}{k_B T}\right) + \exp\left(\frac{-\epsilon_2}{k_B T}\right) + \exp\left(\frac{-\epsilon_3}{k_B T}\right) + \dots} \\ &= \frac{\exp\left(\frac{-\epsilon_i}{k_B T}\right)}{1 + \exp\left(\frac{-\Delta\epsilon}{k_B T}\right) + \exp\left(\frac{-2\Delta\epsilon}{k_B T}\right) + \exp\left(\frac{-3\Delta\epsilon}{k_B T}\right) + \dots} \\ &= \left[1 - \exp\left(\frac{-\Delta\epsilon}{k_B T}\right)\right] \exp\left(\frac{-\epsilon_i}{k_B T}\right) \end{aligned}$$

The limiting value of this fraction when  $T \rightarrow \infty$  is zero; this is because the molecules are now distributed evenly among an infinite number of levels.

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**\*15.48.** Deduce the following from the Sackur-Tetrode equation (Eq.(15.159)), which applies to an ideal monatomic gas:

- a. The dependence of entropy on relative molecular mass  $M_r$ ; also, obtain an expression for  $dS_m/dM_r$ .
- b. The dependence of heat capacity  $C_p$  on relative molecular mass.
- c. The dependence of entropy on temperature; also obtain an expression for  $dS_m/dT$ .

**Solution:**

Given: ideal monatomic gas

Required: deduction from the Sackur-Tetrode equation

$$\text{a. } S_m = \text{constant} + \frac{3}{2} R \ln M_r \quad (1)$$

$$\boxed{\frac{dS_m}{dM_r} = \frac{3}{2} \frac{R}{M_r}} \quad (2)$$

- b. The heat capacity of  $C_p$  is  $(\partial H/\partial T)_p = (\partial S/\partial \ln T)_p$  and therefore does not depend on  $M_r$ . The Sackur-Tetrode equation can be written as

$$S_m = \text{constant} + \frac{5}{2} R \ln T \quad (3)$$

and therefore

$$C_{p,m} = \frac{5}{2} R \quad (4)$$

There is no dependence on  $M_r$ .

c. From Eq. (3),

$$\boxed{\frac{dS_m}{dT} = \frac{5 R}{2 T}} \quad (5)$$

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**\*15.49.** Molecules absorbed on a surface sometimes behave like a two-dimensional gas. Derive an equation, analogous to the Sackur-Tetrode Eq. (15.159), for the molar entropy of such an adsorbed layer of atoms, in terms of the molecular mass  $m$  and the surface area  $A$ . What would be the molar entropy if  $10^{10}$  argon atoms were adsorbed on an area of  $1 \text{ cm}^2$  at  $25^\circ\text{C}$ ?

**Solution:**

Given: see above,  $10^{10}$  argon atoms,  $A = 1 \text{ cm}^2$ ,  $T = 25^\circ\text{C}$

Required: derivation for the molar entropy, molar entropy

For two-dimensional translational motion,

$$q_t = \frac{2\pi m k_B T A}{h^2}$$

$$\ln Q = N \ln \left( \frac{q}{N} \right) + N = N \ln \left( \frac{A}{N h^2} 2\pi m k_B T \right) + N$$

$$S + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_A + k_B \ln Q$$

$$S_m = RT \times \frac{1}{T} + R + R \ln \left( \frac{A}{N h^2} 2\pi m k_B T \right)$$

$$S_m = 2R + R \ln \left( \frac{2\pi m k_B T A}{N h^2} \right)$$

$$\text{For Ar, } m = \frac{39.948 \cancel{\text{g}} \cancel{\text{mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{g}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}} = 6.633\,676\,519 \times 10^{-26} \text{ kg}$$

If  $10^{10}$  molecules are absorbed on an area of  $1 \text{ cm}^2$  at  $25^\circ\text{C}$ ,



$$S_m = 2 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \ln \left[ 2\pi \times 6.633\,676\,519 \times 10^{-26} \text{ kg} \right. \\ \left. \times \frac{1.381 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \times 10^{-4} \text{ m}^2 \times 298.15 \text{ K}}{10^{10} \times (6.626 \times 10^{-34})^2 \text{ m}^4 \text{ kg}^2 \text{ s}^{-2}} \right]$$

$$S_m = 16.629 \text{ J K}^{-1} \text{ mol}^{-1} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \ln(3.908\,947\,05 \times 10^7)$$

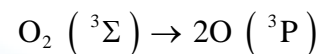
$$S_m = 161.977\,798\,4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{S_m = 162.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**15.50.** Calculate the dissociation constant  $K_c$  for the reaction



at 1 000 K expressing the answer in mole  $l^{-1}$ . Ignore nuclear degeneracy. Use the data from the table of Problem 51, along with the value  $\Lambda_o = 1.25 \times 10^{-9}$  cm.

**Solution:**

Given:  $T = 1\,000$  K, table of Problem 51,  $\Lambda_o = 1.25 \times 10^{-9}$  cm

Required:  $K_c$

The calculation here is

For our case:



$$E_{\text{O}_2}^o = -D_0 = -5.08 \text{ eV}$$

$$K_p^1 = \frac{q_{\text{O}}^2}{q_{\text{O}_2} N} \exp\left(-\frac{D_o}{kT}\right)$$

$$q_{\text{O}_2} = q_t q_r q_v q_e \quad \text{and} \quad q_{\text{O}} = q_t q_e$$

$$q_{\text{O}_2} = q_t q_r q_v q_e = \left( \frac{4\pi m_{\text{O}_2} k_B T}{h^2} \right)^{3/2} \left( \frac{T}{2\Theta_r} \right) \left( \frac{1}{1 - e^{-\Theta_v/T}} \right) \times \overset{\text{triplet state degeneracy}}{\tilde{3}}$$

$$q_{\text{O}_2} = \left( \frac{4\pi \times 32 \times 1.673 \times 10^{-27} \times 1.381 \times 10^{-23} \times 1000}{(6.626 \times 10^{-34})^2} \right)^{3/2} \\ \times \left( \frac{1000}{2 \times 2.07} \right) \left( \frac{1}{1 - e^{-2230/1000}} \right) \times \overset{\text{triplet state degeneracy}}{\underset{3}{3}}$$

$$q_{\text{O}_2} = (6.6129 \times 10^{20})^{3/2} (241.54)(9.23)(3) = 1.137 \times 10^{35} \text{ m}^{-3}$$

and

$$q_{\text{O}} = q_i q_e = \frac{1}{\left( 1.25 \times 10^{-9} \text{ cm} \times 0.01 \frac{\text{m}}{\text{cm}} \right)^3} (3) = 6.788 \times 10^{16} \text{ m}^{-3}$$

so

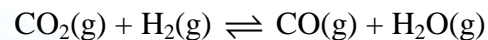
$$K_p^1 = \frac{q_{\text{O}}^2}{q_{\text{O}_2} N} \exp\left(-\frac{D_o}{k_B T}\right) = \\ = \left( \frac{(6.788 \times 10^{16})^2}{(1.137 \times 10^{35})(6.022 \times 10^{23})} \right) \left( \frac{(\text{m}^{-3})^2}{\text{m}^{-3}} \right) \\ \times \exp\left(-\frac{5.08 \text{ eV} \times 1.602 \times 10^{-19} \text{ J eV}^{-1}}{1.381 \times 10^{-23} \times 1000}\right) \\ = (1.34 \times 10^{-25}) \overbrace{\exp(-58.929)}^{2.555 \times 10^{-26}} = 3.43 \times 10^{-51} \text{ molecule}^{-1} \frac{l}{\text{m}^3} \times 10^6 \frac{\text{m}^3}{l} \\ = 3.43 \times 10^{-51} \text{ molecule}^{-1} = 2.063 \times 10^{-27} \text{ mol}^{-1}$$

This is  $K_p^1$ , to get  $K_c^1 = K_p^1 \times (RT)^{-1}$

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**15.51.** From the data in Table 15.5, calculate  $K_p$  at 1000 K for the “water-gas” reaction



**Solution:**

Given: Table 15.5,  $T = 1000$  K

Required:  $K_p$

$$\Delta H_{298}^{\circ} = -110.53 - 241.82 + 393.51 = 41.16 \text{ kJ mol}^{-1} \text{ (from Table 15.5)}$$

$$\Delta(H_{298}^{\circ} - H_0^{\circ}) = 8.665 + 9.902 - 8.468 - 9.360 = 0.739 \text{ kJ mol}^{-1}$$

$$\Delta H_0^{\circ} = 41.16 - 0.739 = 40.421 \text{ kJ mol}^{-1}$$

$$\Delta G_{1000}^{\circ} = 40\,420 - 1000(204.18 + 196.83 - 226.54 - 137.07) = 3020 \text{ J mol}^{-1}$$

$$\ln K_p = -\frac{3020}{8.3145 \times 1000} = -0.363\,220\,879$$

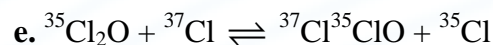
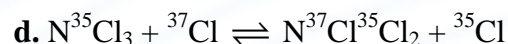
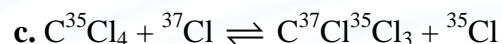
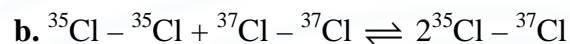
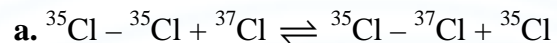
$$K_p = 0.695\,432\,809$$

$$\boxed{K_p = 0.695}$$

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**15.52.** Without making detailed calculations but by using symmetry numbers, estimate the equilibrium constants for the following reactions:



(Because of the similarity of the masses, these estimates will be quite accurate.)

D. M. Bishop and K. J. Laidler, *J. Chem. Phys.*, 42, 1688(1965), have defined a *statistical factor* for a reaction as the number of equivalent ways in which a reaction can occur. Thus for reaction (a) from left to right the statistical factor is 2, since the  $^{37}\text{Cl}$  atom can abstract either of the two  $^{37}\text{Cl}$  atoms. For the reverse reaction the statistical factor  $r$  is 1, since the  $^{35}\text{Cl}$  atom can only abstract the  $^{35}\text{Cl}$  atom in order to give the desired products. If two identical molecules are involved, the statistical factor must be taken as the number of equivalent products divided by 2; thus for reaction (b) from right to left the statistical factor is  $\frac{1}{2}$ .

Bishop and Laidler proved that the ratio  $l/r$  of statistical factors is always equal to the ratio  $\sigma_A\sigma_B/\sigma_Y\sigma_Z$  of symmetry numbers. Verify that this is true for the given reactions.

This statistical factor procedure is useful in providing a simple insight into the factors that appear in equilibrium constants.

**Solution:**

Given: above reactions

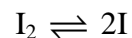
Required: equilibrium constants

The symmetry numbers are given below the molecules (They are 1 for atoms.) and the statistical factors are shown above and below the arrows; for simplicity  $^{35}\text{Cl}$  is written as Cl and  $^{37}\text{Cl}$  as Cl\*.

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**\*15.53.** Calculate the equilibrium constant at 1000 °C for the dissociation



given the following information: moment of inertia of  $\text{I}_2 = 7.426 \times 10^{-45} \text{ kg m}^2$ , wavenumber for  $\text{I}_2$  vibration =  $213.67 \text{ cm}^{-1}$ ,  $\Delta U_0 = 148.45 \text{ kJ mol}^{-1}$ . The I atom is in a  $^2\text{P}_{3/2}$  state; neglect higher states.

**Solution:**

Given: above reaction,  $T = 1000 \text{ °C}$ ,  $\text{I}_2 = 7.426 \times 10^{-45} \text{ kg m}^2$ , wavenumber for  $\text{I}_2$  vibration =  $213.67 \text{ cm}^{-1}$ ,  $\Delta U_0 = 148.45 \text{ kJ mol}^{-1}$ ,  $^2\text{P}_{3/2}$  state

Required: equilibrium constant

Mass of I atom,

$$m = \frac{126.90 \cancel{\text{ g}} \cancel{\text{ mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{ g}^{-1}}}{6.022 \times 10^{23} \cancel{\text{ mol}^{-1}}} = 2.107\,273\,331 \times 10^{-25} \text{ kg}$$

From Eq. 15.86, the translational partition function for the I atom, with  $V = 1 \text{ m}^3$ , is

$$q_t = \frac{(2\pi m k_B T)^{3/2} V}{h^3}$$

$$q_t(\text{I}) = \frac{\left(2\pi \times 2.107\,273\,331 \times 10^{-25} \cancel{\text{ kg}} \times 1.381 \times 10^{-23} \cancel{\text{ m}^2} \cancel{\text{ kg}} \cancel{\text{ s}^{-2}} \cancel{\text{ K}^{-1}}\right)^{3/2}}{\left(6.626 \times 10^{-34}\right)^3 \cancel{\text{ m}^6} \cancel{\text{ kg}^3} \cancel{\text{ s}^{-3}}} \times (1273.15 \text{ K})^{3/2} \times 1 \cancel{\text{ m}^3}$$

$$q_t(\text{I}) = 1.221 \times 10^{34}$$

The degeneracy of the ground state is

$$2\left(\frac{3}{2}\right) + 1 = 4$$

Thus

$$q_t(\text{I}) = 4 \times 1.221 \times 10^{34} = 4.884 \times 10^{34}$$

For the iodine molecule,

$$q_t(\text{I}_2) = \frac{\left(2\pi \times 2 \times 2.107\,273\,331 \times 10^{-25} \cancel{\text{kg}} \times 1.381 \times 10^{-23} \cancel{\text{m}^2} \cancel{\text{kg}} \cancel{\text{s}^{-2}} \cancel{\text{K}^{-1}}\right)^{3/2}}{\left(6.626 \times 10^{-34}\right)^3 \cancel{\text{m}^6} \cancel{\text{kg}^3} \cancel{\text{s}^{-3}}} \\ \times (1273.15 \text{ K})^{3/2} \times 1 \cancel{\text{m}^3} \\ q_t(\text{I}_2) = 2^{3/2} q_t(\text{I}) = 3.453 \times 10^{34}$$

From Eq. 15.95,

$$q_r = \frac{2Ik_{\text{B}}T}{\sigma h^2} \\ q_r(\text{I}_2) = \frac{8\pi^2 \times 7.426 \times 10^{-45} \cancel{\text{kg}} \cancel{\text{m}^2} \times 1.381 \times 10^{-23} \cancel{\text{m}^2} \cancel{\text{kg}} \cancel{\text{s}^{-2}} \cancel{\text{K}^{-1}} \times 1273.15 \text{ K}}{2 \left(6.626 \times 10^{-34}\right)^2 \cancel{\text{m}^4} \cancel{\text{kg}^2} \cancel{\text{s}^{-2}}} \\ q_r(\text{I}_2) = 1.174 \times 10^4$$

And from Eq. 15.102,

$$q_v = \frac{1}{1 - \exp\left(\frac{-h\nu}{k_B T}\right)}$$

$$q_v(I_2) = \frac{1}{1 - \exp\left(\frac{-6.626 \times 10^{-34} \times 21\,367.0 \times 2.998}{10^{-8} \times 1.381 \times 10^{-23} \times 1273.15}\right)}$$

$$q_v(I_2) = \frac{1}{1 - 0.785\,520\,326}$$

$$q_v(I_2) = 4.662\,446\,486$$

The molecular partition function for  $I_2$  is thus

$$q_{I_2} = 3.453 \times 10^{34} \times 1.174 \times 10^4 \times 4.662\,446\,486$$

$$q_{I_2} = 1.890\,072\,814 \times 10^{39}$$

From Eq. 15.140, the molecular equilibrium constant,  $K$ , is

$$K^\circ = \frac{q_Y q_Z}{q_A q_B} N^{-\sum \nu} \exp\left(\frac{-\Delta U_0}{RT}\right)$$

$$K^\circ = \frac{(4.884 \times 10^{34})^2}{1.890\,072\,814 \times 10^{39}} \exp\left(\frac{-148\,450 \times 1273.15}{8.3145}\right)$$

$$K^\circ = (1.262\,038\,998 \times 10^{30})(8.120 \times 10^{-7})$$

$$K^\circ = 1.025\,362\,665 \times 10^{24}$$

Its value in molar units is

$$K_c = 1.025\,362\,665 \times 10^{24} \frac{\text{molecule}}{\text{m}^3} \times \frac{1}{6.022 \times 10^{23}} \frac{\text{molecule}^{-1}}{\text{mol}}$$

$$K_c = 1.702\,694\,562 \text{ mol m}^{-3} = 1.702\,694\,562 \times 10^{-3} \text{ mol dm}^{-3}$$



At  $T = 1273.15 \text{ K}$ ,  $1 \text{ mol dm}^{-3} = 105.8 \text{ bar}$

$$K_p = 1.702\,694\,562 \times 10^{-3} \frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3}} \times \frac{105.8 \text{ bar}}{1 \text{ mol dm}^{-3}}$$

$$K_p = 0.180\,257\,057 \text{ bar}$$

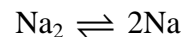
$$\boxed{K_p = 0.180 \text{ bar}}$$

(The experimental value obtained by Starck and Bodenstein in 1910 was  $0.165 \text{ atm} = 0.167 \text{ bar}$ .)

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**\*15.54.** Calculate the equilibrium constant  $K_P$  for the dissociation



at 1000 K, using the following data: internuclear separation in  $\text{Na}_2 = 0.3716 \text{ nm}$ , vibrational wavenumber  $\tilde{\nu} = 159.2 \text{ cm}^{-1}$ ,  $\Delta U_0 = 70.4 \text{ kJ mol}^{-1}$ . The Na atom is in a  $^2\text{S}_{1/2}$  state; neglect higher states.

**Solution:**

Given:  $T = 1000 \text{ K}$ , internuclear separation in  $\text{Na}_2 = 0.3716 \text{ nm}$ , vibrational wavenumber  $\tilde{\nu} = 159.2 \text{ cm}^{-1}$ ,  $\Delta U_0 = 70.4 \text{ kJ mol}^{-1}$ ,  $^2\text{S}_{1/2}$  state

Required:  $K_P$

Mass of Na atom is:

$$m = \frac{22.99 \cancel{\text{ g mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{ g}^{-1}}}{6.022 \times 10^{23} \cancel{\text{ mol}^{-1}}} = 3.817\,668\,549 \times 10^{-26} \text{ kg}$$

The electronic partition function is  $2\left(\frac{1}{2}\right) + 1 = 2$ .

The molecular partition function for Na is

$$q(\text{Na}) = \frac{2 \times (2\pi \times 3.817\,668\,549 \times 10^{-26} \times 1.381 \times 10^{-23} \times 1000)^{3/2}}{(6.626 \times 10^{-34})^3}$$

$$q(\text{Na}) = 1.311 \times 10^{33}$$

For  $\text{Na}_2$ ,

$$q_t(\text{Na}_2) = \frac{(2\pi \times 2 \times 3.818 \times 10^{-26} \times 1.381 \times 10^{-23} \times 1000)^{3/2}}{(6.626 \times 10^{-34})^3}$$

$$q_t(\text{Na}_2) = 1.854 \times 10^{33} \quad (= q_t(\text{Na}) \times \sqrt{2})$$

Moment of inertia of Na<sub>2</sub> is,

$$I = \frac{3.817\,668\,549 \times 10^{-26} \times (0.3716 \times 10^{-9})^2}{2}$$

$$I = 2.636\,072\,43 \times 10^{-45} \text{ kg m}^2$$

$$q_r(\text{Na}_2) = \frac{8\pi^2 \times 2.636 \times 10^{-45} \times 1.381 \times 10^{-23} \times 1000}{2 \times (6.626 \times 10^{-34})^2}$$

$$q_r(\text{Na}_2) = 3273.466\,428$$

$$q_v(\text{Na}_2) = \frac{1}{1 - \exp\left(\frac{-159.2 \times 2.998 \times 10^{10} \times 6.626 \times 10^{-34}}{1.381 \times 10^{-23} \times 1000}\right)}$$

$$q_v(\text{Na}_2) = 4.885\,909\,311$$

Thus, the partition function of Na<sub>2</sub> at 1000 K is

$$= 1.854 \times 10^{33} \times 3273.466\,428 \times 4.885\,909\,311$$

$$= 2.965\,261\,662 \times 10^{37}$$

The molecular equilibrium constant is

$$K = \frac{(1.311 \times 10^{33})^2}{2.965\,261\,662 \times 10^{37}} \exp\left(\frac{-70\,400}{8.3145 \times 1000}\right)$$

$$K = 1.218\,742\,727 \times 10^{25}$$

$$K_c = 1.218\,742\,727 \times 10^{25} \frac{\text{molecule m}^{-3}}{\text{molecule m}^{-3}} \times \frac{1}{6.022 \times 10^{23}} \frac{\text{molecule}^{-1}}{\text{molecule}^{-1}} \text{ mol}$$

$$K_c = 20.238\,172\,16 \text{ mol m}^{-3} = 0.020\,238\,172\,16 \text{ mol dm}^{-3}$$

At  $T = 1000 \text{ K}$ ,  $1 \text{ mol dm}^{-3} = 83.1 \text{ bar}$

$$K_p = 0.020\,238\,172\,16 \cancel{\text{mol dm}^{-3}} \times \frac{83.1 \text{ bar}}{\cancel{\text{mol dm}^{-3}}}$$

$$K_p = 1.681\,792\,106 \text{ bar}$$

$$\boxed{K_p = 1.68 \text{ bar}}$$

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**\*15.55.** Calculate the equilibrium constant  $K_P$  at 1200 K for  $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ , from the following data: internuclear separation in  $\text{Cl}_2 = 199 \text{ pm}$ , wavenumber for vibration  $= 565.0 \text{ cm}^{-1}$ ,  $\Delta U_0 = 240.0 \text{ kJ mol}^{-1}$ . The ground state of Cl is a doublet,  $^2\text{P}_{\frac{3}{2}, \frac{1}{2}}$ , the separation between the states being  $881 \text{ cm}^{-1}$ .

**Solution:**

Given:  $T = 1200 \text{ K}$ , internuclear separation in  $\text{Cl}_2 = 199 \text{ pm}$ , wavenumber for vibration  $= 565.0 \text{ cm}^{-1}$ ,  $\Delta U_0 = 240.0 \text{ kJ mol}^{-1}$ ,  $^2\text{P}_{\frac{3}{2}, \frac{1}{2}}$ , separation between states  $= 881 \text{ cm}^{-1}$ .

Required:  $K_P$

Mass of Cl atom is

$$m = \frac{35.45 \cancel{\text{ g}} \cancel{\text{ mol}^{-1}} \times 10^{-3} \text{ kg } \cancel{\text{ g}^{-1}}}{6.022 \times 10^{23} \cancel{\text{ mol}^{-1}}} = 5.886\,748\,589 \times 10^{-26} \text{ kg}$$

Translational partition function for the Cl atom with  $V = 1 \text{ m}^3$ , is

$$Q_t(\text{Cl}) = \frac{(2\pi \times 5.886\,748\,589 \times 10^{-26} \times 1.381 \times 10^{-23} \times 1200)^{3/2}}{(6.626 \times 10^{-34})^3}$$

$$Q_t(\text{Cl}) = 1.651 \times 10^{33}$$

The degeneracy of the  $^2\text{P}_{3/2}$  state is 4; that of the  $^2\text{P}_{1/2}$  is 2; the electronic partition function is thus,

$$Q_e(\text{Cl}) = 4 + 2 \exp\left(\frac{-\epsilon}{k_B T}\right)$$

$$Q_e(\text{Cl}) = 4 + 2 \exp\left(\frac{-881 \times 2.998 \times 10^{10} \times 6.626 \times 10^{-34}}{1.381 \times 10^{-23} \times 1200}\right)$$

$$Q_e(\text{Cl}) = 4.695\,654\,774$$

The complete partition function for the Cl atom is thus

$$Q(\text{Cl}) = 1.651 \times 10^{33} \times 4.695\,654\,774$$

$$Q(\text{Cl}) = 7.752\,526\,032 \times 10^{33}$$

For the  $\text{Cl}_2$  molecule,

$$q_r(\text{Cl}_2) = 2^{3/2} q_r(\text{Cl}) = 4.669\,733\,183 \times 10^{33}$$

The moment of inertia of  $\text{Cl}_2$  is

$$I = \mu r^2 = \frac{1}{2} m_{\text{Cl}} r^2 = \frac{1}{2} \times 5.886\,748\,589 \times 10^{-26} \times (1.99 \times 10^{-10})^2 \text{ kg m}^2$$

$$I = 1.165\,605\,654 \times 10^{-45} \text{ kg m}^2$$

The rotational partition function of  $\text{Cl}_2$  ( $\sigma = 2$ ) is

$$q_r(\text{Cl}_2) = \frac{8\pi^2 \times 1.165\,605\,654 \times 10^{-45} \times 1.381 \times 10^{-23} \times 1200}{2(6.626 \times 10^{-34})^2}$$

$$q_r(\text{Cl}_2) = 1736.934\,508$$

The vibrational partition function is

$$q_r(\text{Cl}_2) = \frac{1}{1 - \exp\left(\frac{-565 \times 2.998 \times 10^{10} \times 6.626 \times 10^{-34}}{1.381 \times 10^{-23} \times 1200}\right)}$$

$$q_r(\text{Cl}_2) = 2.032\,545\,566$$

The molecular partition function of  $\text{Cl}_2$  is thus,

$$q(I_2) = 4.669\,733\,183 \times 10^{33} \times 1736.934\,508 \times 2.032\,545\,566$$

$$q(I_2) = 1.648\,601\,918 \times 10^{37}$$

The molecular equilibrium constant is thus

$$K = \frac{(7.752\,526\,032 \times 10^{33})^2}{1.648\,601\,918 \times 10^{37}} \exp\left(\frac{-240\,000}{8.3145 \times 1200}\right)$$

$$K = 1.303\,447\,699 \times 10^{20}$$

Its value in molar units is

$$K_c = 1.303\,447\,699 \times 10^{20} \frac{\text{molecule}^{-3}}{\text{molecule}^{-3}} \times \frac{1}{6.022 \times 10^{23}} \frac{\text{molecule}^{-1}}{\text{mol}} \text{mol}$$

$$K_c = 2.164\,476\,419 \times 10^{-4} \text{ mol m}^{-3} = 2.164\,476\,419 \times 10^{-7} \text{ mol dm}^{-3}$$

At 1200 K,  $1 \text{ mol dm}^{-3} = 99.8 \text{ bar}$

$$K_p = 2.164\,476\,419 \times 10^{-7} \text{ mol dm}^{-3} \times \frac{99.8 \text{ bar}}{\text{mol dm}^{-3}}$$

$$K_p = 2.160\,147\,466 \times 10^{-5} \text{ bar}$$

$$\boxed{K_p = 2.16 \times 10^{-5} \text{ bar}}$$

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**15.56.** Calculate the isotopic ratio  $K_{\text{H}}/K_{\text{D}}$  at 300 K for the reactions



Take the zero-point energies of  $\text{H}_2$  and  $\text{D}_2$  to be  $26.1 \text{ kJ mol}^{-1}$  and  $18.5 \text{ kJ mol}^{-1}$ , respectively.

**Solution:**

Given:  $T = 300 \text{ K}$ ,  $E_{0,\text{H}_2} = 26.1 \text{ kJ mol}^{-1}$ ,  $E_{0,\text{D}_2} = 18.5 \text{ kJ mol}^{-1}$

Required:  $K_{\text{H}}/K_{\text{D}}$

The equilibrium constant,  $K_{\text{H}}$ , is

$$\frac{q_{\text{H}}^2}{q_{\text{H}_2}} \exp\left(\frac{-E_0}{RT}\right)$$

$q_{\text{H}}$  (translational only) involves  $m_{\text{H}}^{1.5}$

$q_{\text{H}_2}$  (translational and two degrees of rotational freedom) involves  $m_{\text{H}}^{2.5}$ . The preexponential factor in the expression for the equilibrium is thus proportional to  $m^{0.5}$ . The isotope ratio is thus



$$\frac{K_H}{K_D} = \left(\frac{1}{2}\right)^{0.5} \exp\left[\frac{-(26.1+18.5) \text{ kJ mol}^{-1}}{RT}\right]$$
$$\frac{K_H}{K_D} = \left(\frac{1}{2}\right)^{0.5} \exp\left[\frac{-44\,600 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}\right]$$
$$\frac{K_H}{K_D} = 0.707\,106\,781 \times 1.716\,471\,994 \times 10^{-8}$$
$$\frac{K_H}{K_D} = 1.213\,728\,986 \times 10^{-8}$$

$$\frac{K_H}{K_D} = 1.21 \times 10^{-8}$$

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**15.57.** On the basis of transition-state theory, make rough estimates of the preexponential factors at 300 K for the following types of gas reactions:

- a. A bimolecular reaction between an atom and a diatomic molecule, with the formation of a linear activated complex.
- b. A bimolecular reaction between two diatomic molecules, the activated complex being nonlinear with one degree of restricted rotation.
- c. A bimolecular reaction between two nonlinear molecules, the activated complex being nonlinear with no restricted rotation.
- d. A trimolecular reaction between three diatomic molecules, the activated complex being nonlinear with one degree of restricted rotation.

Take the translational partition functions (for three degrees of freedom) to be  $10^{33} \text{ m}^{-3}$ , the rotational functions for each degree of freedom to be 10, the function for a restricted rotation to be 10, and the vibrational functions to be unity. Express the calculated preexponential factors in molecular units ( $\text{m}^3 \text{ s}^{-1}$ ) and in molar units ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

**Solution:**

Given: above gas reactions,  $T = 300 \text{ K}$ , translational partition function =  $10^{33} \text{ m}^{-3}$ , rotational functions = 10, function for restricted rotation = 10, vibrational functions = 1

Required: estimates of the preexponential factors

At 300 K,  $\frac{k_B T}{h} = 6.25 \times 10^{12} \text{ s}^{-1}$ , which for present purposes is rounded to  $6 \times 10^{12} \text{ s}^{-1}$ .

- a. For the atom the partition function is  $10^{33} \text{ m}^{-3}$ . The diatomic molecule has three degrees of translational freedom (which will be written as  $t^3$ ), two degrees of rotational freedom ( $r^2$ ), and one of vibrational freedom ( $v$ ). Its partition function is thus  $10^{33} \times 10^2 = 10^{35} \text{ m}^{-3}$ .

The linear triatomic activated complex has  $t^3$ ,  $r^2$ , and  $v^3$ , and its partition function is

$$10^{33} \times 10^2 = 10^{35} \text{ m}^{-3}$$

The estimated preexponential factor is

$$\frac{k_B T}{h} \frac{q}{q_A q_B} = 6 \times 10^{12} \text{ s}^{-1} \frac{10^{35} \text{ m}^{-3}}{10^{33} \times 10^{35} \text{ m}^{-6}}$$

$$\frac{k_B T}{h} \frac{q}{q_A q_B} = 6 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$$

Multiplication by  $6 \times 10^{23} \text{ mol}^{-1}$  and by  $1000 \text{ dm}^3 \text{ m}^{-3}$  gives

$$\boxed{A = 4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

b. Diatomic molecule A:  $t^3 r^2 v$

$$q_A = q_B = 10^{33} \times 100 = 10^{35} \text{ m}^{-3}$$

Activated complex:  $t^3 r^3 (rr) v^4$  (One vibration has been replaced by a restricted rotation  $[rr]$ .)

$$q = 10^{33} \times 10^4 = 10^{37} \text{ m}^{-3}$$

Thus

$$A = 6 \times 10^{12} \frac{10^{37} \text{ m}^{-3}}{(10^{35})^2} = 6 \times 10^{-21} \text{ m}^{-3} \text{ s}^{-1}$$

$$A = 6 \times 10^{-21} \text{ m}^{-3} \text{ s}^{-1} \times 6 \times 10^{23} \text{ mol}^{-1}$$

$$A = 3600 \text{ m}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$$

$$\boxed{A = 4 \times 10^6 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}}$$

c. (The numbers of vibrational modes are now unspecified, but this makes no difference since they are unity.)

$$\text{Reactants A and B: } t^3 r^3 \quad q = 10^{33} \times 10^3 = 10^{36} \text{ m}^{-3}$$

$$\text{Activated complex: } t^3 r^3 \quad q = 10^{36} \text{ m}^{-3}$$

$$A = 6 \times 10^{12} \frac{10^{36}}{(10^{36})^2} = 6 \times 10^{-24} \text{ m}^{-3} \text{ s}^{-1}$$

$$\boxed{A = 4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

d. Reactants A, B, and C:  $t^3 r^3$        $q = 10^{36} \text{ m}^{-3}$

Activated complex:  $t^3 r^3 (rr)$        $q = 10^{37} \text{ m}^{-3}$

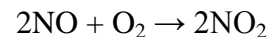
$$A = 6 \times 10^{12} \frac{10^{37}}{(10^{36})^3} = 6 \times 10^{-59} \text{ m}^{-6} \text{ s}^{-1}$$

$$\boxed{A = 4 \times 10^{-29} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

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**15.58.** The rate constant for the reaction



has been found to be proportional to  $T^{-3}$ . Suggest an explanation for this behavior.

**Solution:**

Given: above reaction, rate constant  $\sim T^{-3}$

Required: explanation

The fact that there is no exponential dependence suggests that  $E_0 = 0$ . The temperature dependence arises entirely from the preexponential terms. For each of the three linear reactants there are three degrees of translational freedom and two of rotation, and they vary with temperature as (see Table 15.4)

$$T^{1.5}T = T^{2.5}$$

The activated complex is presumably nonlinear, and if there is no restricted rotation the temperature dependence is as

$$T^{1.5}T^{1.5} = T^3$$

The preexponential factor is thus proportional to

$$T \times \frac{T^3}{(T^{2.5})^3} = T^{-3.5}$$

To explain the dependence on  $T^{-3}$  we must allow the activated complex to have one degree of restricted rotation, so that its partition function is proportional to

$$T^{1.5}T^{1.5}T^{0.5} = T^{3.5}$$

The preexponential factor is then proportional to

$$T \times \frac{T^{3.5}}{(T^{2.5})^3} = T^{-3}$$

We can postulate an activated complex of the following structure

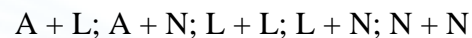


with restricted rotation about the O—O bond.

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**15.59.** Deduce the temperature dependency of the preexponential factor of the following types of reactions, where A represents an atom, L a linear molecule, and N a nonlinear molecule:



**Solution:**

Given: above types of reactions

Required: temperature dependency of the preexponential factor

The temperature dependencies of the partition function are as follows:

$$A: \quad t^3 \quad : \quad T^{1.5}$$

$$L: \quad t^3 r^2 \quad : \quad T^{1.5} T = T^{2.5}$$

$$N: \quad t^3 r^3 \quad : \quad T^{1.5} T^{1.5} = T^3$$

The nonlinear activated complexes have partition functions proportional to  $T^{1.5} T^{1.5} = T^3$ . The temperature dependencies for the various types of reactions are therefore as follows:

$$A + L: \quad \frac{TT^3}{T^{1.5}T^{2.5}} = T^0$$

$$A + N: \quad \frac{TT^3}{T^{1.5}T^3} = T^{-0.5}$$

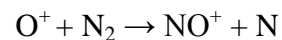
$$L + L: \quad \frac{TT^3}{T^{2.5}T^{2.5}} = T^{-1}$$

$$L + N: \quad \frac{TT^3}{T^{2.5}T^3} = T^{-1.5}$$

$$N + N: \quad \frac{TT^3}{T^3T^3} = T^{-2}$$

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**15.60.** The rate of the reaction

has been found over a certain temperature range to be proportional to  $T^{-0.5}$  (M. McFarland et al., *J. Chem. Phys.*, 59, 6620(1973). How can this be explained in terms of simple transition-state theory?

**Solution:**

Given: above reaction, reaction rate  $\sim T^{-0.5}$

Required: explanation

For the preceding problem it was shown that for an atom reacting with a linear molecule, the preexponential factor is proportional to  $T^0$  if the activated complex is nonlinear. If the activated complex is linear the temperature dependence is  $\frac{TT^{2.5}}{T^{1.5}T^{2.5}} = T^{-0.5}$ . It thus appears that the activated complex is linear, and that the temperature dependence is due entirely to the preexponential factor.

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**15.61.** For the case of two atoms giving a product,  $A + B \rightleftharpoons [AB]^\ddagger \rightarrow \text{Product}$ , show that transition-state theory yields essentially the same expression for the rate constant as the collision theory expression of Eq. (9.76).

**Solution:**

Given: above reaction

Required: prove the above statement

Starting with Eq. 15.152, we get

$$k = \left( \frac{k_B T}{h} \right) \frac{q^\ddagger}{q_A q_B} \exp \left( \frac{-E_0}{k_B T} \right),$$

where

$$q^\ddagger = \frac{[2\pi(m_A + m_B)k_B T]^{3/2}}{h^3} \left( \frac{2Ik_B T}{\hbar^2} \right)$$

$$q_A = \frac{(2\pi m_A k_B T)^{3/2}}{h^3}; \quad q_B = \frac{(2\pi m_B k_B T)^{3/2}}{h^3}$$

Substituting the partition functions in the first equation, where  $I = \left( \frac{m_A m_B}{m_A + m_B} \right) (r_A + r_B)^2 = \mu d_{AB}^2$ , and simplifying, we get

$$k = d_{AB}^2 \left( \frac{8\pi k_B T}{\mu} \right)^{1/2} \exp \left( \frac{-E_0}{k_B T} \right),$$

Which, when multiplied by the Avogadro constant (and also multiplying the numerator and denominator of the argument of the exponential term with the Avogadro constant), is essentially the same as Eq. (9.76).

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**15.62.** In mass-spectrometric experiments, P. Kebarle and coworkers (*J. Chem. Phys.*, 52, 212(1970)) have found that under certain conditions the rate constant for the reaction



is proportional to  $T^{-2.5}$ . Suggest an explanation for this behavior.

**Solution:**

Given: above reaction, reaction rate  $\sim T^{-2.5}$

Required: explanation

The partition function for the ion  $\text{N}^+$  is proportional to  $T^{1.5}$ , while that for  $\text{N}_2$  is proportional to  $T^{2.5}$ . If the activated complex is nonlinear, its partition function is proportional to  $T^3$ . The temperature dependence of the preexponential factor is thus, according to transition-state theory,

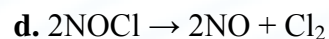
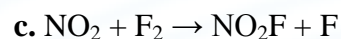
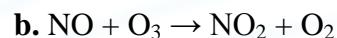
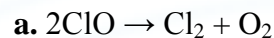
$$\frac{TT^3}{T^{1.5}(T^{2.5})^2} = T^{-2.5},$$

The results can therefore be explained in terms of a nonlinear complex, with  $E_0 = 0$ .

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**15.63.** On the basis of transition-state theory, and assuming the vibrational partitions to be temperature-independent, deduce the temperature dependence of the preexponential factor for each of the following reactions:



**Solution:**

Given: above reactions

Required: deduce temperature dependence of the preexponential factor

The activated complexes will be assumed in all cases to be linear and to have no restricted rotation. If an activated complex is linear, the temperature dependence decreases by 0.5, while each degree of restricted rotation increases the dependence by 0.5.

a.  $\frac{TT^3}{(T^{2.5})^2} = T^{-1}$

b.  $\frac{TT^3}{T^{2.5}T^3} = T^{-1.5}$

c.  $\frac{TT^3}{T^3T^{2.5}} = T^{-1.5}$

d.  $\frac{TT^3}{(T^3)^2} = T^{-2}$

e.  $\frac{TT^3}{(T^{1.5})^3} = T^{-0.5}$

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**15.64.** Benzaldehyde is oxidized by permanganate in aqueous solution. Suppose that the aldehydic hydrogen atom is replaced by a deuterium atom; what can be said on the basis of transition-state theory about the kinetic isotope ratio  $k_{\text{H}}/k_{\text{D}}$  at 25 °C? The wavenumber of the aldehydic C—H vibration is  $2900\text{ cm}^{-1}$ .

**Solution:**

Given: above information,  $T = 25\text{ °C}$ ,  $\lambda = 2900\text{ cm}^{-1}$ .

Required: see above

The two molecules differ only by isotopic substitution and will have different vibrational frequencies for the bond where substitution occurs. We make the reasonable assumption that the change in nuclear mass will not affect the electronic energy and therefore the force constant,  $k$ , will remain the same. The only difference occurs when the reduced mass of the two forms enter the equations. The reduced mass is given by Eq. 13.94 or 13.118, from which the reduced mass of the deuterated form is found to be smaller than that of the form with the normal hydrogen.

Then from Eq. 13.123, the smaller value of  $\mu_{\text{D}}$  makes  $\nu_0$  for the deuterated bond greater than  $\nu_0$  for the hydrogen bond. Consequently, the bond energy of the deuterated form is greater than that of the hydrogen form. This has the effect of putting the deuterated form at a lower potential energy than the hydrogen form, and therefore causing a greater expenditure of energy to promote the deuterated form to the activated state. Therefore the C—H cleavage is greater than that of the C—D bond for the same energy input and the reaction rate of the C—H form should be faster.

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**15.65.** A transition-state theory study of the reaction  $\text{O}(^3\text{P}) + \text{HCl}$  generated the following information at  $T = 600 \text{ K}$ :

*Reactants*

O	$q_t$	$1.767 \times 10^{32} \text{ m}^{-3}$	(for 3 degrees of freedom)
HCl	$q_t$	$6.084 \times 10^{32} \text{ m}^{-3}$	(for 3 degrees of freedom)
	$q_r$	39.40	(for 2 degrees of freedom)
	$\tilde{\nu}_0$	$2991.0 \text{ cm}^{-1}$	

*Transition state (bent)*

	$q_t$	$1.050 \times 10^{33} \text{ m}^{-3}$	(for 3 degrees of freedom)
	$q_r$	1730	(for 3 degrees of freedom)
	$\tilde{\nu}_1$	$1407.9 \text{ cm}^{-1}$	
	$\tilde{\nu}_2$	$266.8 \text{ cm}^{-1}$	

The maximum of the reaction path is at  $45.97 \text{ kJ mol}^{-1}$ . Calculate the rate constant at this temperature.

(Note: Some interesting problems on transition-state theory involving the use of a computer are to be found in S. J. Moss and C. J. Coady, *J. Chem. Ed.*, 60, 455(1983).)

**Solution:**

Given:  $T = 600 \text{ K}$ , above information,

Required: rate constant

Since the vibrational partition functions are not given, we calculate them below:

$$q_v^{\text{HCl}} = \left[ 1 - \exp\left(\frac{-hc \times 2991.0}{k_B T}\right) \right]^{-1} = 1.000\,784\,342,$$

$$q_{v_1}^\ddagger = \left[ 1 - \exp\left(\frac{-hc \times 1407.9}{k_B T}\right) \right]^{-1} = 1.035\,752\,093,$$

$$q_{v_2}^\ddagger = \left[ 1 - \exp\left(\frac{-hc \times 266.8}{k_B T}\right) \right]^{-1} = 2.120\,407\,02.$$

Now, the quantity  $E_0$  appearing in the exponent of Eq. 15.152 has to be evaluated. This is the energy difference between the zero point energy of the reactants and that of the transition state,

$$E_0 = 45\,970 + \frac{1}{2} Lhc (1407.9 + 266.8 - 2991.0) = 38\,097 \text{ J mol}^{-1}.$$

Therefore, we calculate

$$k = \left( \frac{k_B T}{h} \right) \frac{(1.050 \times 10^{33})(1730)(1.035\,752\,093 \times 2.120\,407\,02)}{(1.767 \times 10^{32})(6.084 \times 10^{32})(39.4)(1.000\,784\,342)} \exp\left(\frac{-38\,097}{RT}\right)$$

$$k = 5.677\,833\,797 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$$

$$k = 5.678 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$$

The translational partition functions are calculated for unit volume and hence, although strictly speaking, their units are simply  $\text{m}^{-3}$ , we may interpret this to mean “state  $\text{m}^{-3}$ ” or molecules  $\text{m}^{-3}$ .

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CHAPTER

# 16

The Solid State

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LAIDLER . MEISER . SANCTUARY

## Physical Chemistry

Electronic Edition

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# Problems and Solutions



**Chapter 16****Crystal Lattices, Unit Cells, Density**

**16.1.** How many basis groups are there in

- a. An end-centered lattice;
- b. A primitive lattice?

[Solution](#)

**16.2.** How many lattice points are there in a unit cell of

- a. A face-centered lattice;
- b. A body-centered lattice?

[Solution](#)

- \*16.3.** a. Determine the efficiency of area utilization in packing circles onto the lattice points of a square lattice.  
b. Compare that value with the efficiency of packing circles onto a triangular lattice.  
c. Which packing uses area more efficiently and by how much?

[Solution](#)

- 16.4.** a. Calculate the percentage of free space (volume of the cell minus the volume of the atoms in the unit cell) in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors.  
b. Using the calculated values, determine which of the three structures represents the most efficient packing (least amount of used space).

[Solution](#)

- 16.5.** Derive an equation to relate the density  $D$  of a right-angled unit cell to its edge lengths  $a$ ,  $b$ , and  $c$  and the number of formula units  $z$  per unit cell.

[Solution](#)

**16.6.** Silver crystallizes in a face-centered cubic unit cell with a silver atom on each lattice point.

- a. If the edge length of the unit cell is  $4.0862 \text{ \AA}$ , what is the atomic radius of silver?
- b. Calculate the density of silver.

[Solution](#)

**16.7.** Barium crystallizes with an edge length of  $5.025 \text{ \AA}$  in a body-centered cubic unit cell.

- a. Calculate the atomic radius of barium using this information.
- b. Calculate the density of barium.

[Solution](#)

**16.8.** Aluminum crystallizes in a face-centered cubic lattice with an aluminum atom on each lattice point with the edge length of the unit cell equal to  $4.0491 \text{ \AA}$ .

- a. Calculate the atomic radius of aluminum.
- b. Determine the density of aluminum.

[Solution](#)

**16.9.** Crystals of *p*, *p*'-dibromo- $\alpha$ ,  $\alpha$ '-difluorostilbene  $[\text{BrC}_6\text{H}_4\text{C}(\text{F})=]_2$  are orthorhombic with edge lengths  $a = 28.32 \text{ \AA}$ ;  $b = 7.36 \text{ \AA}$ ;  $c = 6.08 \text{ \AA}$ . If there are four molecules in a unit cell, calculate the density of the crystal.

[Solution](#)

**16.10.** How many formula units exist in pure crystalline Si, which occurs in a face-centered cubic lattice, if its density is  $2.32899 \text{ g cm}^{-3}$  and its cell length is  $a = 356.68 \text{ \AA}$ ? The atomic mass of Si is  $28.0855 \text{ g mol}^{-1}$ .

[Solution](#)

- 16.11.** Sodium chloride crystallizes in a face-centered cubic lattice with four NaCl units per unit cell. If the edge length of the unit cell is 5.629 Å, what is the density of the crystal? Compare your answer to the value given in the *CRC Handbook*.

[Solution](#)

- 16.12.** LiH crystallizes with a face-centered cubic structure. The edge length of the unit cell of LiH is 4.08 Å. Assume anion-anion contact to calculate the ionic radius of H<sup>-</sup>. Compare your answer to the value using the radius of Li<sup>+</sup> as 0.68 Å.

[Solution](#)

- 16.13.** KCl is tetramolecular and crystallizes in a face-centered cubic lattice. If the edge length is 6.278 Å, what is the density of KCl? Compare your answer to the value in the *CRC Handbook*.

[Solution](#)

- 16.14.** Calcium Fluoride crystallizes in a face-centered cubic lattice where  $a = b = c$ , and it has a density of 3.18 g cm<sup>-3</sup>. Calculate the unit cell length for CaF<sub>2</sub>.

[Solution](#)

### Miller Indices and the Bragg Equation

- 16.15.** Calculate the Miller indices of the parallel planes in a cubic lattice that intercepts the unit cell length at  $x = a$ ,  $y = \frac{1}{2}a$ , and  $z = \frac{2}{3}a$ .

[Solution](#)

- 16.16.** Determine the distance (i.e.  $d$  value) of the closest plane parallel to the 100, 110, and 111 faces of the cubic lattice.

[Solution](#)

**16.17.** What are the Miller indices of the plane that cuts through the crystal axes at

- a.  $(2a, b, 3c)$ ;
- b.  $(2a, -3b, 2c)$ ;
- c.  $(a, b, -c)$ ;

[Solution](#)

**16.18.** Determine the value of  $d_{hkl}$  in terms of the cell constants and angles for

- a. The orthorhombic unit cell,
- b. The tetragonal unit cell.

[Solution](#)

**16.19.** Calculate the separation between planes in a cubic lattice with unit cell length of 389 pm when the indices are

- a. 100;
- b. 111;
- c.  $12\bar{1}$

[Solution](#)

**16.20.** Copper sulfate single crystals are orthorhombic with unit cells of dimensions  $a = 488$  pm,  $b = 666$  pm,  $c = 832$  pm. Calculate the diffraction angle from Cu  $K_\alpha$  X rays ( $\lambda = 154.18$  pm) for first-order reflections from the (100), (010), and (111) planes.

[Solution](#)

**16.21.** Determine the angle of reflection when copper  $K_\alpha$  radiation (0.154 18 nm) is incident on a cubic crystal with a lattice constant  $d_{hkl}$  of 0.400 nm.

[Solution](#)

**16.22.** Single crystals of  $\text{FeSO}_4$  are orthorhombic with unit cell dimensions  $a = 482$  pm,  $b = 684$  pm,  $c = 867$  pm. Calculate the diffraction angle from  $\text{Te } K_\alpha$  X rays ( $\lambda = 45.5$  pm) from the (100), (010), and (111) planes

[Solution](#)

**16.23.** Single crystals of  $\text{Hg}(\text{CN})_2$  are tetragonal with unit cell dimensions  $a = 967$  pm and  $c = 892$  pm. Calculate the first-order diffraction angles from the (100) and (111) planes when  $\text{Cu } K_\alpha$  X rays ( $\lambda = 154$  pm) are used.

[Solution](#)

**16.24.** A two-dimensional lattice is depicted in Figure 16.1 with planes superimposed on it parallel to the third direction. Determine the Miller indices for each set of planes representing the external habit of the left-hand crystal.

[Solution](#)

**16.25.** The layers of atoms in a crystal are separated by 325 pm. At what angle in a diffractometer will diffraction occur using

a. molybdenum  $K_\alpha$  X rays ( $\lambda = 70.8$  pm);

b. copper  $K_\alpha$  X rays ( $\lambda = 154$  pm)?

[Solution](#)

**16.26.** Calculate the wavelength of an electron that is accelerated through a potential difference of approximately 40 kV.

[Solution](#)

### Interpretation of X-Ray Data

**16.27.** Find the X-ray wavelength that would give a second-order reflection ( $n = 2$ ) with a  $\theta$  angle of  $10.40^\circ$  from planes with a spacing of  $4.00 \text{ \AA}$ .

[Solution](#)

**16.28.** A substance forms cubic crystals. A powder pattern shows reflections that have either all even or all odd indices. What type of unit cell does it have?

[Solution](#)

**16.29.** A powder pattern of a cubic material has lines that index as (110), (200), (220), (310), (222), (400). What is its type of unit cell?

[Solution](#)

**\*16.30.** The successive  $\sin^2\theta$  values obtained from a powder pattern for  $\alpha$ -Fe are 1, 2, 3, 4, 5, 6, 7, 8, 9, etc.

a. If iron is in the cubic system, which type of unit cell is present?

b. If a copper X-ray tube is used ( $\lambda = 154.18$  pm), calculate the length of the side of the unit cell and the value of  $\theta$  from (100) planes. The density of  $\alpha$ -Fe is  $7.90$  g cm<sup>-3</sup>.

c. What is the radius of the iron atom if the central atom in the cubic cell is assumed to be in contact with the corner atoms?

[Solution](#)

**16.31.** Potassium metal has a density of  $0.856$  g cm<sup>-3</sup> and has a body-centered cubic lattice. Calculate the length of the unit cell  $a$  and the distance between (200), (110), and (222) planes. Potassium has an atomic mass of  $39.102$  g mol<sup>-1</sup>.

[Solution](#)

**16.32.** Low-angle lines in the Cu  $K_\alpha$  powder pattern of KCl are found to be at  $\theta = 14.18^\circ$ ,  $20.25^\circ$ , and  $25.10^\circ$ . Find the crystal type from these data. (For Cu  $K_\alpha$   $\lambda = 154.18$  pm.) What other information is needed for a definitive determination?

[Solution](#)

**16.33.** The smallest observed diffraction angle of silver taken with Cu  $K_\alpha$  radiation ( $\lambda = 154.18$  pm) is  $19.176^\circ$ . This angle is associated with the (111) plane in the cubic close-packed structure of silver.

a. Determine the value of the unit cell length  $a$ .

b. If  $D(\text{Ag}) = 10.500$  g cm<sup>-3</sup> and  $M = 107.87$  g mol<sup>-1</sup>, calculate the number of atoms in the unit cell.

[Solution](#)

- 16.34.** Sodium fluoride is known to form a cubic closed-packed structure. The smallest angle obtained with Cu  $K_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) is  $16.72^\circ$  and is derived from the (111) planes. Find the value of  $a$ , the unit cell parameter.

[Solution](#)

- 16.35.** The X-ray powder pattern of NaCl is taken with a chromium tube giving Cr  $K_\alpha = 229.1 \text{ pm}$ . The  $\theta$  values of the lines are:  $20^\circ 36'$ ,  $23^\circ 58'$ ,  $35^\circ 4'$ ,  $42^\circ 21'$ ,  $44^\circ 43'$ ,  $54^\circ 20'$ ,  $62^\circ 17'$ ,  $65^\circ 16'$ . From these data determine the value of each  $d_{hkl}$  and index the lines. From the  $hkl$  values, show that this is a face-centered system.

[Solution](#)

### Bonding in Crystals and Metals

- 16.36.** Cadmium sulfide has been used as a yellow pigment by artists. The sulfide crystallizes with cadmium occupying  $\frac{1}{2}$  of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of cadmium sulfide?

[Solution](#)

- 16.37.** Rutile is a mineral that contains titanium and oxygen. The structure of rutile may be described as a closest-packed array of oxygen atoms with titanium in  $\frac{1}{2}$  of the octahedral holes. What is the formula of rutile? What is the oxidation number of titanium?

[Solution](#)

- 16.38.** A tetrahedral hole is shown in Figure 16.33. Determine the largest sphere of radius  $r$  that can fit into a tetrahedral hole when the surrounding four spherical atoms of the lattice are in contact. Let the lattice atom have radius  $R$ .

[Solution](#)

- 16.39.** An octahedral hole is surrounded by six spheres of radius  $R$  in contact. If one-sixth of each of the six coordinating spheres contributes to the volume of the octahedron surrounding the hole, calculate the maximum radius of the sphere that can be accommodated.

[Solution](#)



- 16.40.** Calculate the value of  $\Delta E_c$  of the RbBr from the following information:  $\Delta_f H = -414 \text{ kJ mol}^{-1}$ ;  $I$  (ionization energy, Rb) =  $397 \text{ kJ mol}^{-1}$ ;  $\Delta_{\text{sub}} H(\text{Rb}) = 84 \text{ kJ mol}^{-1}$ ;  $D_0(\text{Br}_2) = 192 \text{ kJ mol}^{-1}$ ;  $A$  (electron affinity, Br) =  $318 \text{ kJ mol}^{-1}$ .

[Solution](#)

### Supplementary Problems

- 16.41.** Some of the  $d$  spacings for the mineral canfieldite ( $\text{Ag}_8\text{SnS}_6$ ) are 3.23, 3.09, 3.04, 2.81, and 2.74 Å obtained with Cu  $K_\alpha$  X rays ( $\lambda = 1.5418 \text{ Å}$ ).

- Find the corresponding angles of diffraction.
- This is a cubic system with  $a = 21.54 \text{ Å}$ ; determine the  $hkl$  values for the first 3  $d$  spacings.

[Solution](#)

- 16.42.** A copper selenide mineral ( $\text{Cu}_5\text{Se}_4$ ) called athabascaite is orthorhombic with  $a = 8.277$ ,  $b = 11.982$ ,  $c = 6.441$ . Strong intensity lines using Cu  $K_\alpha$  X rays ( $\lambda = 154.18 \text{ pm}$ ) are observed at  $12.95^\circ$ ,  $13.76^\circ$ , and  $14.79^\circ$ . Determine the  $d$  spacings and assign  $hkl$  values to these lines.

[Solution](#)

- \*16.43.** Zinc blende is the face-centered cubic form of ZnS with Zn at  $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}$ ;

$\frac{1}{2}, \frac{1}{2}, 0$  and with S at  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}$ .

- Determine the structure factor from the (111) planes that gives rise to the lowest angle reflection at  $\theta = 14.30^\circ$  using Cu  $K_\alpha$  ( $\lambda = 154.18 \text{ pm}$ ).
- Calculate the dimension  $a$  of the unit cell.

[Solution](#)



**16.44.** Calculate the Debye temperature of tungsten that is isotropic (an assumption of the Debye model). The cutoff frequency is given by

$$\nu_D = \left( \frac{9N}{4\pi V} \right)^{1/3} \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)^{-1/3}$$

where

$$c_l = 5.2496 \times 10^5 \text{ cm s}^{-1}$$

and

$$c_t = 2.9092 \times 10^5 \text{ cm s}^{-1}$$

are the longitudinal and trasverse elastic wave velocities, respectively, in tungsten.

[Solution](#)

### Essay Questions

- 16.45.** List the 14 Bravais lattices and group them into *P*, *I*, *F*, *C*, and *R* cells.
- 16.46.** Explain why the initial X-ray investigation of the two face-centered cubic structures, NaCl and KCl, showed that NaCl was face centered whereas KCl was simple cubic.
- 16.47.** If  $\Delta H_c$  were required rather than  $\Delta E_c$ , what modification of the Born-Haber cycle would be needed?
- 16.48.** X-ray diffraction is often used to measure residual stress in metals. Suggest that change in the measured parameters allow this determination.
- 16.49.** Gold diffuses faster in lead at 300°C than does sodium chloride in water at 15°C. Point defects based on vacancies can account for such high rates. For an ionic material, suggest ways in which such vacancies can occur without altering the stoichiometry of the crystal.

**Solutions**

**16.1.** How many basis groups are there in

- a. An end-centered lattice;
- b. A primitive lattice?

**Solution:**

Given: see above

Required: number of basis groups

- a. The end-centered lattice has  $\left(\frac{1}{8}\right) \times 8 + \left(\frac{1}{2}\right) \times 2 = 2$  lattice points. Since one basis is a each lattice point, each unit cell has two basis groups.
- b. The primitive lattice has one lattice point and there is therefore only one basis group.

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**16.2.** How many lattice points are there in a unit cell of

- a. A face-centered lattice;
- b. A body-centered lattice?

**Solution:**

Given: see above

Required: number of lattice points

- a. A unit cell has 8 lattice points at the corners of a cube; each corner is shared with seven other unit cells. Therefore, only  $1/8$  of the 8 belong to a particular face-centered cubic (fcc) cell. Each face has an additional lattice point shared between two cells; there are therefore  $\left(\frac{1}{2}\right) \times 6 = 3$  lattice points in the faces. For the unit cell: 1 (from corners) + 3 (from faces) = 4 lattice points.
- b. A body-centered cubic (bcc) lattice has 1 lattice point belonging to the unit cell plus  $\left(\frac{1}{8}\right) \times 8$  corner points. There are thus  $1 + 1 = 2$  lattice points.

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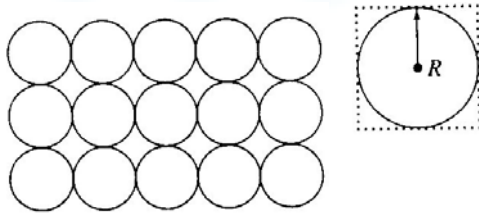
- 16.3.** a. Determined the efficiency of area utilization in packing circles onto the lattice points of a square lattice.  
 b. Compare that value with the efficiency of packing circles onto a triangular lattice.  
 c. Which packing uses area more efficiently and by how much?

**Solution:**

Given: see above

Required: see above

- a. Consider the array of circles:

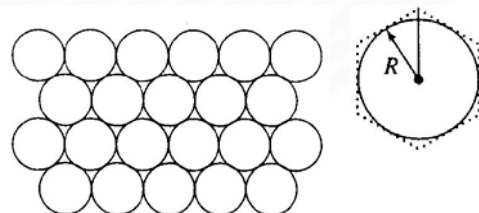


The area belonging to each circle is shown as a dotted box of area  $4R^2$ . The area of the circle is  $\pi R^2$ .

$$\text{efficiency of filling space} = \frac{\pi R^2}{4R^2} = 0.785\,398\,163$$

efficiency of filling space = 0.785 or 78.5%
--

- b. Circles on triangular lattice are shown below:



The hexagonal area belonging to a single circle is shown by the dotted lines. The hexagonal area is made up of 12 right triangles, each having an area of

$$\left(\frac{1}{2}R\right)\left(\frac{1}{\sqrt{3}}R\right) = \left(\frac{1}{2\sqrt{3}}\right)R^2$$

The total area is  $12\left(\frac{1}{2}\sqrt{3}\right)R^2 = 2\sqrt{3}R^2$ , and the efficiency of filling space is given by

$$\frac{\pi R^2}{2\sqrt{3}R^2} = \frac{\pi}{2\sqrt{3}} = 0.906\,899\,682$$

efficiency of filling space = 0.907 or 90.7%
--

c. The triangular form is more efficient by a factor of

$$\frac{90.689\,9682}{78.539\,8163} = 1.154\,700\,538$$

$$= \boxed{1.15}$$

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- 16.4.** a. Calculate the percentage of free space (volume of the cell minus the volume of the atoms in the unit cell) in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors.  
 b. Using the calculated values, determine which of the three structures represents the most efficient packing (least amount of used space).

**Solution:**

Given: see above

Required: see above

- a. A *simple* cubic crystal lattice of side  $2r$  contains one atom of radius  $r$ .  
 Free space = volume of cube – volume of atom

$$\text{Free space} = (2r)^3 - \frac{4}{3}\pi r^3$$

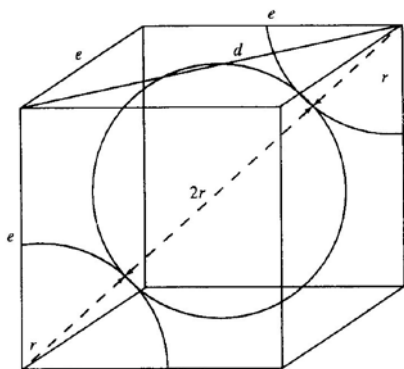
$$\text{Free space} = 8r^3 - 4.188\,790\,205r^3$$

$$\text{Free space} = 3.811\,209\,795r^3$$

$$\text{Percent free space} = \frac{3.811\,209\,795r^3}{8r^3} \times 100 = 47.640\,1224\%$$

Percent free space = 47.64%
-----------------------------

A *body-centered* cube contains two atoms of radius  $r$  in the unit cell. The length of the edge of the cube is calculated using the Pythagorean theorem:



The diagonal of the cube is  $4r$ .

$$(4r)^2 = d^2 + e^2$$

but

$$d^2 = e^2 + e^2$$

so

$$(4r)^2 = 3e^2$$

$$e = \frac{4r}{\sqrt{3}} \text{ (length of edge)}$$

$$\text{Free space} = \left(\frac{4r}{\sqrt{3}}\right)^3 - 2\left(\frac{4}{3}\pi r^3\right)$$

$$\text{Free space} = 12.316\,805\,74r^3 - 8.377\,580\,41r^3$$

$$\text{Free space} = 3.939\,225\,33r^3$$

$$\text{Percent free space} = \frac{3.939\,225\,33}{12.316\,805\,74} \times 100$$

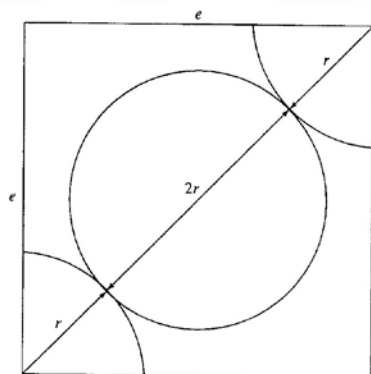
$$\text{Percent free space} = 31.982\,523\,83\%$$

$$\boxed{\text{Percent free space} = 31.98\%}$$

A *face-centered* cube contains four atoms of radius  $r$  in the unit cell. The length of the edge of the cube is calculated using the Pythagorean theorem:

$$(4r)^2 = e^2 + e^2 = 2e^2$$

$$e = 2r\sqrt{2}$$



$$\text{Free space} = (2\sqrt{2}r)^3 - 4\left(\frac{4}{3}\pi r^3\right)$$

$$\text{Free space} = 22.627\,417r^3 - 16.755\,160\,82r^3$$

$$\text{Free space} = 5.872\,256\,18r^3$$

$$\text{Percent free space} = \frac{5.872\,256\,18r^3}{22.627\,417r^3} \times 100 = 25.951\,951\%$$

Percent free space = 25.95%
-----------------------------

- b.** The face-centered cube has the least amount of unused space.

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**16.5.** Derive an equation to relate the density  $D$  of a right-angled unit cell to its edge lengths  $a$ ,  $b$ , and  $c$  and the number of formula units  $z$  per unit cell.

**Solution:**

Given: see above

Required: derive an equation that relates  $D$  to  $a$ ,  $b$ , and  $c$  and  $z$

The volume of a unit cell with right angles is the product  $abc$  of its edges. Since one mole of the crystal contains  $z$  unit cells, the molar volume is  $V_m = \frac{abc}{z}$ . The molar mass  $M$  divided by the molar volume  $V_m$  is the density  $D$ :

$$\frac{M}{V_m} = \frac{\text{kg}}{\text{mol}} \div \left( \frac{\text{m}^3}{\text{atom}} \times N_{av} \right), \text{ where } N_{av} \text{ is the Avogadro's number in } \frac{\text{atom}}{\text{mol}}$$

$$\frac{M}{V_m} = \frac{\text{kg}}{\text{m}^3} = D$$

Therefore,

$$D = \frac{M}{V_m} = \frac{M}{\frac{abcN_{av}}{z}}$$

$$\boxed{D = \frac{Mz}{abcN_{av}}}$$

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**16.6.** Silver crystallizes in a face-centered cubic unit cell with a silver atom on each lattice point.

- a. If the edge length of the unit cell is  $4.0862 \text{ \AA}$ , what is the atomic radius of silver?
- b. Calculate the density of silver.

**Solution:**

Given: characteristic of silver atom, edge length

Required: atomic radius and density

- a. In a face-centered cube containing identical atoms of radius  $r$ , the edge length is  $2r\sqrt{2}$ . For silver, the edge length is  $4.0862 \text{ \AA}$ .

$$\text{Edge length} = 4.0862 \text{ \AA} = 2r\sqrt{2}$$

$$r = \frac{4.0862}{2\sqrt{2}} \text{ \AA}$$

$$r = 1.444\ 689\ 865 \text{ \AA}$$

$$\boxed{r = 1.4447 \text{ \AA}}$$

- b. The volume of a unit cell is

$$V = \left( 4.0862 \text{ \AA} \times \frac{10^{-8} \text{ cm}}{\text{\AA}} \right)^3$$

$$V = 6.822\ 740\ 578 \times 10^{-23} \text{ cm}^3$$

One unit cell contains four atoms, so 1 mol of Ag contains

$$\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}} \times \frac{1 \text{ unit cell}}{4 \text{ atoms}} = 1.5055 \times 10^{23} \text{ unit cells mol}^{-1}$$

The mass of 1 mol of Ag is  $107.8682 \text{ g mol}^{-1}$ . The density is

$$D = \frac{M}{V_m} = \frac{107.8682 \text{ g mol}^{-1}}{(1.5055 \times 10^{23} \text{ cells mol}^{-1})(6.822\,740\,578 \times 10^{-23} \text{ cm}^3)}$$

$$D = 10.501\,559\,89 \text{ g cm}^{-3}$$

$$\boxed{D = 10.512 \text{ g cm}^{-3}}$$

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**16.7.** Barium crystallizes with an edge length of 5.025 Å in a body-centered cubic unit cell.

- a. Calculate the atomic radius of barium using this information.
- b. Calculate the density of barium.

**Solution:**

Given: characteristics of barium, edge length

Required: atomic radius, density

- a. In a body-centered cubic unit cell, the metal atoms are in contact along the diagonal of the cube. The diagonal of the cube forms a right triangle with the unit cell edge and the diagonal of a face. Use the Pythagorean theorem to determine the length of the diagonal,  $d$ , on the face of the cube in terms of  $e$ .

$$d^2 = e^2 + e^2 = 2e^2$$

$$d = \sqrt{2}e$$

The diagonal of the cube is the length of four atomic radii and can be calculated by again using the Pythagorean theorem.

$$(\text{Diagonal})^2 = (4r)^2 = (2e)^2 + e^2$$

$$(\text{Diagonal})^2 = 16r^2 = 3e^2$$

$$\text{Diagonal} = 4r = \sqrt{3}e$$

$$r = \frac{\sqrt{3}e}{4} = \frac{\sqrt{3}}{4}(5.025 \text{ Å}) = 2.175\,888\,827 \text{ Å}$$

$$\boxed{r = 2.176 \text{ Å}}$$

- b. Given a body-centered cubic structure, each unit cell contains two atoms. Use the unit cell edge length to calculate the unit cell volume and the volume occupied by each atom. Multiply to obtain the molar volume and divide the gram atomic weight by this value to obtain density ( $e$  = edge length).

$$V(\text{cell}) = e^3 = (5.025 \times 10^{-8} \text{ cm})^3 = 1.268\,843\,906 \times 10^{-22} \text{ cm}^3$$

$$V(\text{atom}) = \frac{1.268\,843\,906 \times 10^{-22} \text{ cm}^3}{2 \text{ atoms}} = \frac{6.344\,219\,531 \times 10^{-23} \text{ cm}^3}{\text{atom}}$$

$$V(\text{mole}) = \left( \frac{6.344\,219\,531 \times 10^{-23} \text{ cm}^3}{\cancel{\text{atom}}} \right) \times \left( \frac{6.022 \times 10^{23} \cancel{\text{atoms}}}{\text{mol}} \right)$$

$$V(\text{mole}) = \frac{38.204\,890\,02 \text{ cm}^3}{\text{mol}}$$

$$D(\text{Ba}) = \left( \frac{137.33 \text{ g}}{\text{mol}} \right) \div \left( \frac{38.204\,890\,02 \text{ cm}^3}{\text{mol}} \right)$$

$$D(\text{Ba}) = \left( \frac{137.33 \text{ g}}{\cancel{\text{mol}}} \right) \times \left( \frac{\cancel{\text{mol}}}{38.204\,890\,02 \text{ cm}^3} \right)$$

$$D(\text{Ba}) = 3.594\,566\,034 \text{ g cm}^{-3}$$

$$\boxed{D(\text{Ba}) = 3.595 \text{ g cm}^{-3}}$$

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**16.8.** Aluminum crystallizes in a face-centered cubic lattice with an aluminum atom on each lattice point with the edge length of the unit cell equal to  $4.0491 \text{ \AA}$ .

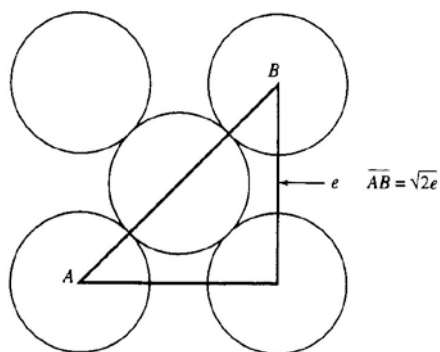
- Calculate the atomic radius of aluminum.
- Determine the density of aluminum.

**Solution:**

Given: characteristics of aluminum, edge length

Required: atomic radius, density

- In a body-centered cubic unit cell, the metal atoms are in contact along the diagonal of the cube. The diagonal of the cube forms a right triangle with the unit cell edge and the diagonal of a face. Use the Pythagorean theorem to determine the length of the diagonal,  $d$ , on the face of the cube in terms of  $e$ .



$$r(\text{Al}) = \frac{\sqrt{2}(4.0491 \text{ \AA})}{4} = 1.431\,573\,034 \text{ \AA}$$

$$\boxed{r(\text{Al}) = 1.432 \text{ \AA}}$$

- Follow the same procedure for density as used in Problem 16.7, but noting that a face-centered cubic cell contains four atoms per cell instead of two.

$$V(\text{cell}) = e^3 = (4.0491 \times 10^{-8} \text{ cm})^3 = 6.638\,584\,809 \times 10^{-23} \text{ cm}^3$$

$$V(\text{mol}) = \frac{6.638\,584\,809 \times 10^{-23} \text{ cm}^3}{\cancel{\text{cell}}} \times \frac{1 \cancel{\text{cell}}}{4 \cancel{\text{atoms}}} \times \frac{6.022 \times 10^{23} \cancel{\text{atoms}}}{\text{mol}}$$

$$V(\text{mol}) = 9.994\,389\,43 \text{ cm}^3 \text{ mol}^{-1}$$

$$D(\text{Al}) = \frac{26.9815 \text{ g}}{\cancel{\text{mol}}} \times \frac{1 \cancel{\text{mol}}}{9.994\,389\,43 \text{ cm}^3} = 2.699\,664\,666 \text{ g cm}^{-3}$$

$$\boxed{D(\text{Al}) = 2.700 \text{ g cm}^{-3}}$$

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**16.9.** Crystals of *p*, *p*'-dibromo- $\alpha$ ,  $\alpha$ '-difluorostilbene  $[\text{BrC}_6\text{H}_4\text{C}(\text{F})=]_2$  are orthorhombic with edge lengths  $a = 28.32 \text{ \AA}$ ;  $b = 7.36 \text{ \AA}$ ;  $c = 6.08 \text{ \AA}$ . If there are four molecules in a unit cell, calculate the density of the crystal.

**Solution:**

Given: see above

Required: density of the crystal

From Problem 16.5:

$$D = \frac{Mz}{abcN_{av}}, \text{ where } N_{av} \text{ is the Avogadro's number and } M \text{ is the molar mass}$$

Molar mass of  $[\text{BrC}_6\text{H}_4\text{C}(\text{F})=]_2 = 373.94 \text{ g mol}^{-1}$

$$D = \frac{4(373.94 \text{ g mol}^{-1})}{(28.32)(7.36)(6.08) \cancel{\text{ \AA}^3} \times (10^{-8} \text{ cm } \cancel{\text{ \AA}^{-1}})^3 \times (6.022 \times 10^{23} \cancel{\text{ mol}^{-1}})}$$

$$D = 1.959 \text{ } 9569 \text{ g cm}^{-3}$$

$$\boxed{D = 1.96 \text{ g cm}^{-3}}$$

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**16.10.** How many formula units exist in pure crystalline Si, which occurs in a face-centered cubic lattice, if its density is  $2.328\,99\text{ g cm}^{-3}$  and its cell length is  $a = 50431\,066\text{ Å}$ ? The atomic mass of Si is  $28.085\,41\text{ g mol}^{-1}$ .

**Solution:**

Given: characteristics of Si, its density, cell length, and atomic mass

Required: number of formula

From Problem 16.5:

$$D = \frac{Mz}{abcN_{av}}, \text{ where } N_{av} \text{ is the Avogadro's number and } M \text{ is the molar mass}$$

For a face-centered cubic lattice, all edge lengths are equal, that is  $a = b = c$ .

$$z = \frac{DabcN_{av}}{M}$$

$$z = \frac{2.328\,99\text{ g cm}^{-3} (5.431\,066\text{ Å})^3 (10^{-8}\text{ cm Å}^{-1})^3 (6.022 \times 10^{23}\text{ mol}^{-1})}{28.085\,41\text{ g mol}^{-1}}$$

$$z = 7.999\,868\,501$$

$$\boxed{z = 8}$$

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**16.11.** Sodium chloride crystallizes in a face-centered cubic lattice with four NaCl units per unit cell. If the edge length of the unit cell is 5.629 Å, what is the density of the crystal? Compare your answer to the value given in the *CRC Handbook*.

**Solution:**

Given: characteristics of sodium chloride, edge length

Required: density

$$D = \frac{Mz}{abcN_{av}}, \text{ where } N_{av} \text{ is the Avogadro's number and } M \text{ is the molar mass}$$

For sodium chloride,  $z = 4$ ,  $M = 58.45$ . As the crystal is a face-centered cubic lattice,

$$a = b = c = 5.629 \text{ Å}$$

$$D = \frac{Mz}{abcN_{av}}$$

$$D = \frac{4(58.45 \text{ g mol}^{-1})}{(5.629 \text{ Å})^3 (10^{-8} \text{ cm Å}^{-1})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$D = 2.176 \text{ 7573 g cm}^{-3}$$

$$\boxed{D = 2.176 \text{ g cm}^{-3}}$$

CRC value = 2.165 g cm<sup>-3</sup> at 25°C

The lower density given in the handbook may be due to voids and other imperfections in the crystal.

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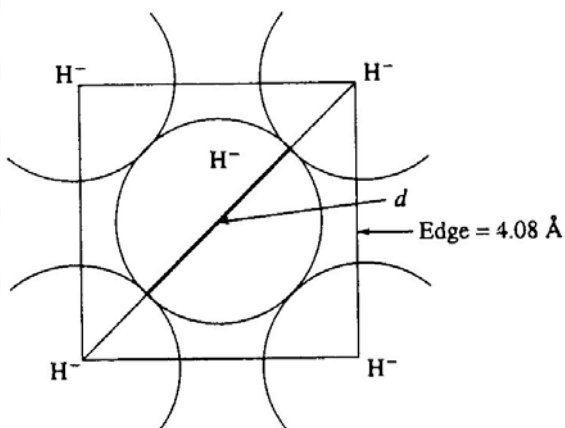
**16.12.** LiH crystallizes with a face-centered cubic structure. The edge length of the unit cell of LiH is  $4.08 \text{ \AA}$ . Assume anion-anion contact to calculate the ionic radius of  $\text{H}^-$ . Compare your answer to the value using the radius of  $\text{Li}^+$  as  $0.68 \text{ \AA}$ .

**Solution:**

Given: LiH characteristics, edge length

Required: ionic radius

The structure is face-centered cubic with the hydride ions in contact along the diagonal of the face as shown in the figure.



From the figure,

$$(4d_{\text{H}^-})^2 = 2(4.08 \text{ \AA})^2$$

$$d_{\text{H}^-} = 1.442\,497\,834 \text{ \AA}$$

$$\boxed{d_{\text{H}^-} = 1.44 \text{ \AA}}$$

Another way to look at this problem is to consider that lithium ions fill the space along the edge, giving an edge length of  $2r_{\text{Li}^+} + 2r_{\text{H}^-}$ . The radius of the hydride ion is computed from the edge length  $e$  and the reported radius of  $\text{Li}^+$  ( $0.68 \text{ \AA}$ ).

$$e = 4.08 \text{ \AA} = 2r_{\text{Li}^+} + 2r_{\text{H}^-}$$

$$e = 2(0.68 \text{ \AA}) + 2r_{\text{H}^-}$$

$$r_{\text{H}^-} = \frac{e - 2(0.68 \text{ \AA})}{2}$$

$$r_{\text{H}^-} = \frac{4.08 \text{ \AA} - 1.36 \text{ \AA}}{2}$$

$$\boxed{r_{\text{H}^-} = 1.36 \text{ \AA}}$$

A recent edition of the *CRC Handbook* gives two values for  $\text{Li}^+$ : with coordination number 4, its radius is  $0.56 \text{ \AA}$ ; with coordination number 6, its radius is  $0.76 \text{ \AA}$ . The value of  $0.68 \text{ \AA}$  just cited is found in an older edition and represents an average value. Any value of  $r_{\text{H}^-}$  will depend upon the value of  $r_{\text{Li}^+}$  used in this method. It is common to consider that the anions are in contact with the cations occupying the open space. There is no requirement that the anions and the cations contact. Therefore, the first method gives a better estimate of the maximum size of  $\text{H}^-$ .

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**16.13.** KCl is tetramolecular and crystallizes in a face-centered cubic lattice. If the edge length is  $6.278 \text{ \AA}$ , what is the density of KCl? Compare your answer to the value in the *CRC Handbook*.

**Solution:**

Given: characteristics of KCl, edge length

Required: density

The molar mass of KCl is  $74.55 \text{ g mol}^{-1}$ .

$$D = \frac{M_z}{abcN_{av}}$$

$$D = \frac{4(74.55 \text{ g mol}^{-1})}{(6.278 \text{ \AA} \times 10^{-8} \text{ cm \AA}^{-1})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$D = 2.001\,257\,414 \text{ g cm}^{-3}$$

$$\boxed{D = 2.001 \text{ g cm}^{-3}}$$

$$\text{CRC value} = 1.984 \text{ g cm}^{-3}$$

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**16.14.** Calcium Fluoride crystallizes in a face-centered cubic lattice where  $a = b = c$ , and it has a density of  $3.18 \text{ g cm}^{-3}$ . Calculate the unit cell length for  $\text{CaF}_2$ .

**Solution:**

Given: characteristics of calcium fluoride, density

Required: unit cell length

The molar mass of calcium fluoride is  $78.08 \text{ g mol}^{-1}$

There are four calcium ions per unit cell and eight associated fluoride ions. Consequently,  $z = 4$  and rearrangement of

$$D = \frac{Mz}{abcN_{av}} \text{ with } a = b = c \text{ gives}$$

$$a^3 = \frac{Mz}{DN_{av}} = \frac{4(78.08 \text{ g mol}^{-1})}{(3.18 \text{ g cm}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$a^3 = 1.630\,917\,245 \times 10^{-22} \text{ cm}^3$$

$$a = 5.463\,580\,021 \times 10^{-8} \text{ cm}$$

$$a = 5.46 \times 10^{-8} \text{ cm} = 5.46 \text{ \AA} = 546 \text{ pm}$$

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**16.15.** Calculate the Miller indices of the parallel planes in a cubic lattice that intercepts the unit cell length at  $x = a$ ,  $y = \frac{1}{2}a$ , and  $z = \frac{2}{3}a$ .

**Solution:**

Given: cubic lattice,  $x = a$ ,  $y = \frac{1}{2}a$ , and  $z = \frac{2}{3}a$ .

Required: Miller indices

The intercepts along the axes are spaces at  $a/h$ ,  $b/k$ ,  $c/l$ . For a cubic system

$$1a = \frac{a}{h}, h = 1; \quad \frac{a}{2} = \frac{a}{k}, k = 2; \quad \frac{2a}{3} = \frac{a}{l}, l = \frac{3}{2}$$

Clearing fraction we have

$$\boxed{(hkl) = (243)}$$

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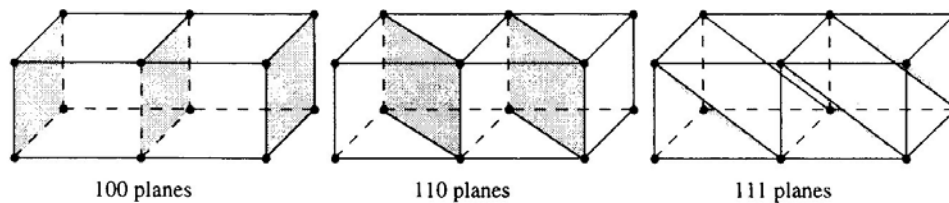
**16.16.** Determine the distance (i.e.  $d$  value) of the closest plane parallel to the 100, 110, and 111 faces of the cubic lattice.

**Solution:**

Given: see above

Required: see above

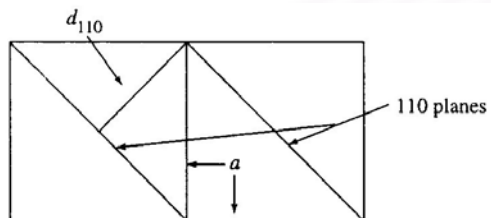
The faces are shown in the figures below:



The spacings are calculated from the formula

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Or from trigonometry as demonstrated from the 110 planes:





$$d_{110}^2 + d_{110}^2 = a^2$$

$$2d_{110}^2 = a^2$$

$$d_{110} = \frac{a}{\sqrt{2}}$$

The results are

$$d_{110} = a \quad d_{110} = \frac{a}{\sqrt{2}} \quad d_{111} = \frac{a}{\sqrt{3}}$$

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**16.17.** What are the Miller indices of the plane that cuts through the crystal axes at

- a.  $(2a, b, 3c)$ ;
- b.  $(2a, -3b, 2c)$ ;
- c.  $(a, b, -c)$ ;

**Solution:**

Given: see above

Required: Miller indices

Originals	Reciprocals	Miller indices
a. $(2a, b, 3c)$	$\frac{1}{2}, 1, \frac{1}{3}$	$(362)$
b. $(2a, -3b, 2c)$	$\frac{1}{2}, -\frac{1}{3}, \frac{1}{2}$	$(3\bar{2}3)$
c. $(a, b, -c)$	$1, 1, -1$	$(11\bar{1})$

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**16.18.** Determine the value of  $d_{hkl}$  in terms of the cell constants and angles for

- a. The orthorhombic unit cell,
- b. The tetragonal unit cell.

**Solution:**

Given: see above

Required: value of  $d_{hkl}$

- a. In the orthorhombic system, all three sides are different and all angles are  $90^\circ$ . Therefore, all sine terms are equal to one and all cosine terms are equal to zero. From Eq. 16.19,

$$d_{hkl}^2 = \frac{1}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

or

$$d_{hkl} = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

- b. For the tetragonal system,  $a = b = c$  and all angles are  $90^\circ$ . Therefore, all sine terms are equal to one and all cosine terms are equal to zero. From Eq. 16.19.

$$d_{hkl}^2 = \frac{1}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

Then with  $a = b$ ,

$$d_{hkl}^2 = \frac{1}{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}$$

or

$$d_{hkl} = \left( \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

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**16.19.** Calculate the separation between planes in a cubic lattice with unit cell length of 389 pm when the indices are

a. 100;

b. 111;

c.  $12\bar{1}$

**Solution:**

Given: see above

Required: separation between planes

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

a.  $d_{100} = \frac{389 \text{ pm}}{1}$   
 $d_{100} = 389 \text{ pm}$

b.  $d_{111} = \frac{389 \text{ pm}}{(1^2 + 1^2 + 1^2)^{1/2}} = \frac{389 \text{ pm}}{\sqrt{3}}$   
 $d_{111} = 224.589 \text{ } 254 \text{ } 7 \text{ pm}$   
 $d_{111} = 225 \text{ pm}$

c.  $d_{12\bar{1}} = \frac{389 \text{ pm}}{[1^2 + 2^2 + (-1)^2]^{1/2}} = \frac{389 \text{ pm}}{\sqrt{6}}$   
 $d_{12\bar{1}} = 158.808 \text{ } 585 \text{ pm}$   
 $d_{12\bar{1}} = 159 \text{ pm}$

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**16.20.** Copper sulfate single crystals are orthorhombic with unit cells of dimensions  $a = 488$  pm,  $b = 666$  pm,  $c = 832$  pm. Calculate the diffraction angle from Cu  $K_\alpha$  X rays ( $\lambda = 154.18$  pm) for first-order reflections from the (100), (010), and (111) planes.

**Solution:**

Given: characteristics of copper sulfate, cell dimensions,  $\lambda = 154.18$  pm, planes indices.

Required: diffraction angle.

$$\lambda = 2d_{hkl} \sin \theta \quad \lambda = 154 \text{ pm}$$

From Problem 16.18,

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\frac{1}{d_{100}^2} = \frac{1}{a^2}; d_{100} = a = 488 \text{ pm}$$

$$\frac{1}{d_{010}^2} = \frac{1}{b^2}; d_{010} = b = 666 \text{ pm}$$

$$\frac{1}{d_{111}^2} = \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} = \frac{1}{488^2} + \frac{1}{666^2} + \frac{1}{832^2}$$

$$\frac{1}{d_{111}^2} = 4.199\,140\,016 \times 10^{-6} + 2.254\,506\,759 \times 10^{-6} + 1.144\,619\,083 \times 10^{-6}$$

$$\frac{1}{d_{111}^2} = 7.898\,265\,858 \times 10^{-6}$$

$$d_{111} = 355.823\,089\,3 \text{ pm}$$

$$\sin \theta = \frac{\lambda}{2d_{100}} = \frac{154 \text{ pm}}{2(488 \text{ pm})} = 0.157\,786\,885$$

$$\theta_{100} = 9.078\,462\,401^\circ$$

$$\boxed{\theta_{100} = 9.08^\circ}$$

$$\sin \theta = \frac{\lambda}{2d_{010}} = \frac{154 \text{ pm}}{2(666 \text{ pm})} = 0.115\,615\,615$$

$$\theta_{010} = 6.639\,134\,078^\circ$$

$$\boxed{\theta_{010} = 6.64^\circ}$$

$$\sin \theta = \frac{\lambda}{2d_{111}} = \frac{154 \text{ pm}}{2(356 \text{ pm})} = 0.216\,292\,134$$

$$\theta_{111} = 12.491\,345\,05^\circ$$

$$\boxed{\theta_{111} = 12.49^\circ}$$

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**16.21.** Determine the angle of reflection when copper  $K_\alpha$  radiation (0.154 18 nm) is incident on a cubic crystal with a lattice constant  $d_{hkl}$  of 0.400 nm.

**Solution:**

Given:  $\lambda = 0.154\ 18\ \text{nm}$ ,  $d_{hkl} = 0.400\ \text{nm}$

Required: angle of reflection

Assuming a first-order reflection,

$$\lambda = 2d \sin \theta$$

$$0.154\ 18\ \cancel{\text{nm}} = 2(0.400\ \cancel{\text{nm}}) \sin \theta$$

$$\sin \theta = 0.192\ 725$$

$$\theta = 11.111\ 854\ 97^\circ$$

$$\boxed{\theta = 11.1^\circ}$$

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**16.22.** Single crystals of  $\text{FeSO}_4$  are orthorhombic with unit cell dimensions  $a = 482$  pm,  $b = 684$  pm,  $c = 867$  pm. Calculate the diffraction angle from  $\text{Te } K_{\alpha}$  X rays ( $\lambda = 45.5$  pm) from the (100), (010), and (111) planes

**Solution:**

Given: characteristics of  $\text{FeSO}_4$  crystal, cell dimensions,  $\lambda = 45.5$  pm, plane indices

Required: diffraction angle

$$\lambda = 2d_{hkl} \sin\theta \quad \lambda = 45.5 \text{ pm}$$

From Eq. 16.19 or Problem 16.18,

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\frac{1}{d_{100}^2} = \frac{1}{a^2}; d_{100} = a = 482 \text{ pm}$$

$$\frac{1}{d_{010}^2} = \frac{1}{b^2}; d_{010} = b = 684 \text{ pm}$$

$$\frac{1}{d_{111}^2} = \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} = \frac{1}{482^2} + \frac{1}{684^2} + \frac{1}{867^2}$$

$$\frac{1}{d_{111}^2} = 4.304\,333\,603 \times 10^{-6} + 2.137\,409\,801 \times 10^{-6} + 1.330\,337\,413 \times 10^{-6}$$

$$\frac{1}{d_{111}^2} = 7.772\,080\,818 \times 10^{-6}$$

$$d_{111} = 358.699\,974\,7 \text{ pm}$$

$$\sin \theta = \frac{\lambda}{2d_{100}} = \frac{45.5 \text{ pm}}{2(482 \text{ pm})} = 0.047\,199\,17$$

$$\theta_{100} = 2.705\,318\,347^\circ$$

$$\boxed{\theta_{100} = 2.71^\circ}$$

$$\sin \theta = \frac{\lambda}{2d_{010}} = \frac{45.5 \text{ pm}}{2(684 \text{ pm})} = 0.033\,260\,233$$

$$\theta_{010} = 1.906\,022\,56^\circ$$

$$\boxed{\theta_{010} = 1.91^\circ}$$

$$\sin \theta = \frac{\lambda}{2d_{111}} = \frac{45.5 \text{ pm}}{2(359 \text{ pm})} = 0.063\,370\,473$$

$$\theta_{111} = 3.633\,295\,227^\circ$$

$$\boxed{\theta_{111} = 3.63^\circ}$$

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**16.23.** Single crystals of  $\text{Hg}(\text{CN})_2$  are tetragonal with unit cell dimensions  $a = 967$  pm and  $c = 892$  pm. Calculate the first-order diffraction angles from the (100) and (111) planes when  $\text{Cu } K_\alpha$  X rays ( $\lambda = 154$  pm) are used.

**Solution:**

Given: characteristics of  $\text{Hg}(\text{CN})_2$  crystal, cell dimensions,  $\lambda = 154$  pm, plane indices

Required: first-order diffraction angles

$$\lambda = 2d_{hkl} \sin\theta \quad \lambda = 154 \text{ pm}$$

From Eq. 16.19 or Problem 16.18,

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

$$\frac{1}{d_{100}^2} = \frac{1}{a^2}; d_{100} = a = 967 \text{ pm}$$

$$\frac{1}{d_{111}^2} = \frac{1^2 + 1^2}{967^2} + \frac{1^2}{892^2}$$

$$\frac{1}{d_{111}^2} = 2.138\,833\,844 \times 10^{-6} + 1.256\,811\,921 \times 10^{-6}$$

$$d_{111} = 542.673\,745\,5 \text{ pm}$$

$$\sin \theta = \frac{\lambda}{2d_{100}} = \frac{154 \text{ pm}}{2(967 \text{ pm})} = 0.079\,627\,714$$

$$\theta_{100} = 4.567\,167\,086^\circ$$

$$\boxed{\theta_{100} = 4.57^\circ}$$

$$\sin \theta = \frac{\lambda}{2d_{111}} = \frac{154 \text{ pm}}{2(543 \text{ pm})} = 0.141\,804\,788$$

$$\theta_{111} = 8.152\,295\,044^\circ$$

$$\boxed{\theta_{111} = 8.15^\circ}$$

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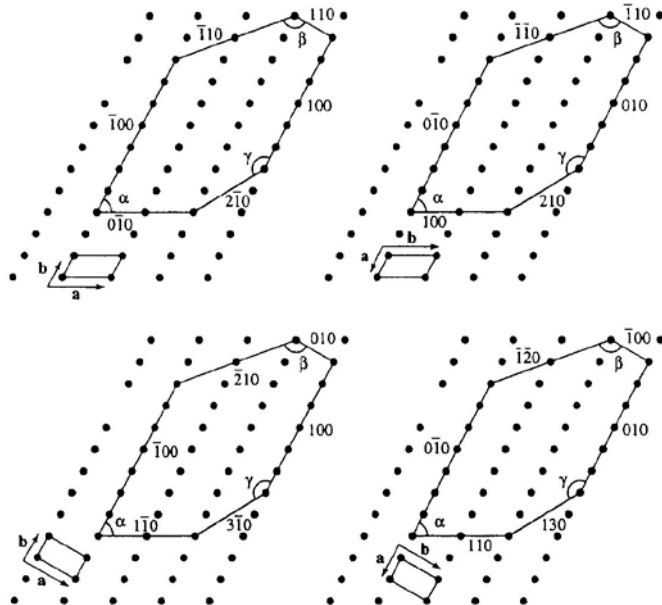
**16.24.** A two-dimensional lattice is depicted in Figure 16.1 with planes superimposed on it parallel to the third direction. Determine the Miller indices for each set of planes representing the external habit of the left-hand crystal.

**Solution:**

Given: figure 16.1

Required: Miller indices

The Miller indices depend upon the way in which we draw the unit cell. Four different ways and their corresponding values are shown. Notice that the right-hand cell has been used for convenience. The planes in the left-hand cell will have exactly the same indices.



Notice that the angle between dots is not exactly  $90^\circ$ . This does not matter since the  $a$  vector that determines the reciprocal lattice will be perpendicular to the actual planes

The indices are A,  $(0, 1, 0)$ ; B,  $(-1, 1, 0)$ ; C,  $(2, 1, 0)$ , and D,  $(1, 1, 0)$ .

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**16.25.** The layers of atoms in a crystal are separated by 325 pm. At what angle in a diffractometer will diffraction occur using

- a. molybdenum  $K_\alpha$  X rays ( $\lambda = 70.8$  pm);
- b. copper  $K_\alpha$  X rays ( $\lambda = 154$  pm)?

**Solution:**

Given: see above

Required: angle of diffraction

- a. Let  $n = 1$  in the Bragg equation  $n\lambda = 2d \sin \theta$

$$\text{Then } \theta = \sin^{-1} \left( \frac{\lambda}{2d} \right)$$

$$\theta = \sin^{-1} \left( \frac{70.8}{2 \times 325} \right)$$

$$\theta = \sin^{-1} (0.108\,923\,076)$$

$$\theta = 6.253\,239\,405^\circ$$

$$\boxed{\theta = 6.25^\circ}$$

b.  $\theta = \sin^{-1} \left( \frac{\lambda}{2d} \right)$

$$\theta = \sin^{-1} \left( \frac{154}{2 \times 325} \right)$$

$$\theta = \sin^{-1} (0.236\,923\,076)$$

$$\theta = 13.705\,008\,73^\circ$$

$$\boxed{\theta = 13.71^\circ}$$

Notice that the shorter the wavelength, the smaller the diffraction angle.

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**16.26.** Calculate the wavelength of an electron that is accelerated through a potential difference of approximately 40 kV.

**Solution:**

Given: see above

Required: wavelength

The kinetic energy of the electron is  $\frac{1}{2}mu^2$  and is also  $VQ$ ; it thus follows that

$$u = \left( \frac{2VQ}{m} \right)^{1/2}$$

$$u = \left( \frac{2(40 \times 10^3 \text{ V})(1.60 \times 10^{-19} \text{ C})}{9.11 \times 10^{-31} \text{ kg}} \right)^{1/2}$$

$$1 \text{ V C} = 1 \text{ J}$$

$$u = (1.405\,049\,396 \times 10^{16} \text{ J kg}^{-1})^{1/2}$$

$$\text{Since } \text{J} = \text{kg m}^2 \text{ s}^{-2}$$

$$u = 1.185347795 \times 10^8 \text{ m s}^{-1}$$

Substituting into the de Broglie equation (Eq. 11.56) gives

$$\lambda = \frac{h}{mu}$$

$$\lambda = \frac{6.63 \times 10^{-34} \text{ J s}}{(9.11 \times 10^{-31} \text{ kg})(1.19 \times 10^8 \text{ m s}^{-1})}$$

$$\lambda = 6.115\,728\,399 \times 10^{-12} \text{ m}$$

$$\boxed{\lambda = 6.12 \text{ pm}}$$

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**16.27.** Find the X-ray wavelength that would give a second-order reflection ( $n = 2$ ) with a  $\theta$  angle of  $10.40^\circ$  from planes with a spacing of  $4.00 \text{ \AA}$ .

**Solution:**

Given:  $n = 2$ ,  $\theta = 10.40^\circ$ , plane spacing =  $4.00 \text{ \AA}$

Required: X-ray wavelength

$$n\lambda = 2d \sin \theta$$

$$\lambda = \frac{2d \sin \theta}{n}$$

$$\lambda = \frac{2(4.00 \text{ \AA})[\sin(10.40^\circ)]}{2}$$

$$\lambda = 0.722\,076\,581 \text{ \AA}$$

$$\boxed{\lambda = 0.722 \text{ \AA}}$$

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**16.28.** A substance forms cubic crystals. A powder pattern shows reflections that have either all even or all odd indices. What type of unit cell does it have?

**Solution:**

Given: see above

Required: type of cell

From Figure 16.28, it is determined that the face-centered cubic (fcc) system is the only one that conforms to the data. Note that the symmetry of the crystal determines which indices will appear.

[image]

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**16.29.** A powder pattern of a cubic material has lines that index as (110), (200), (220), (310), (222), (400). What is its type of unit cell?

**Solution:**

Given: see above, lines indexes

Required: type of unit cell

From Figure 16.28, it can only be bcc

[image]

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**\*16.30.** The successive  $\sin^2\theta$  values obtained from a powder pattern for  $\alpha$ -Fe are 1, 2, 3, 4, 5, 6, 7, 8, 9, etc.

- If iron is in the cubic system, which type of unit cell is present?
- If a copper X-ray tube is used ( $\lambda = 154.18$  pm), calculate the length of the side of the unit cell and the value of  $\theta$  from (100) planes. The density of  $\alpha$ -Fe is  $7.90 \text{ g cm}^{-3}$ .
- What is the radius of the iron atom if the central atom in the cubic cell is assumed to be in contact with the corner atoms?

**Solution:**

Given: see above

Required: see above

- From Figure 16.28, it is seen that the ratio 7 is not allowed for cubic systems. The ratio must be 2, 4, 6, and so on. Consequently, the structure is bcc.
- For a bcc system,  $a = b = c$ ,  $z = 2$ , and from Problem 16.5,  $D = zMa^3L$  or

$$a^3 = \frac{2(55.85 \text{ g mol}^{-1})}{(7.90 \text{ g cm}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$a^3 = 2.347\,931\,004 \times 10^{-23} \text{ cm}^3$$

$$a = 2.863\,486\,304 \times 10^{-8} \text{ cm}$$

$$a = 286.348\,630\,4 \text{ pm}$$

$$\boxed{a = 286 \text{ pm}}$$

For 100 type planes,  $d$  is  $a/2$  since the planes are actually (200). Therefore, from  $2d \sin \theta = n\lambda$ ,

$$\sin \theta = \frac{154.18 \text{ pm}}{286 \text{ pm}} = 0.539\,090\,909$$

$$\theta = 32.621\,774\,51^\circ$$

$$\boxed{\theta = 32.6^\circ}$$

- c. The body diagonal is the smallest interatomic distance and has the value  $\frac{\sqrt{3}a}{2}$ . Therefore, the radius is the distance from the center of one Fe atom to the center of the central atom divided by 2:

$$r_{\text{Fe}} = \frac{\sqrt{3}a}{2 \times 2} = \frac{\sqrt{3} \times 286.348\,630\,4\text{ pm}}{4}$$

$$r_{\text{Fe}} = 123.992\,594\,1\text{ pm}$$

$$\boxed{r_{\text{Fe}} = 124.0\text{ pm}}$$

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**16.31.** Potassium metal has a density of  $0.856 \text{ g cm}^{-3}$  and has a body-centered cubic lattice. Calculate the length of the unit cell  $a$  and the distance between (200), (110), and (222) planes. Potassium has an atomic mass of  $39.102 \text{ g mol}^{-1}$ .

**Solution:**

Given: characteristics of potassium metal, density, plane indices, atomic mass

Required: length of the unit cell, distance between the given planes

There are two atoms in a body-centered lattice and we may write:

$$\text{Density} = \frac{(\text{number of atoms/cell})(\text{atomic mass})}{N_{av}a^3}, \text{ where } N_{av} \text{ is the Avogadro's number}$$

$$0.856 \text{ g cm}^{-3} = \frac{2(39.102 \text{ g mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1})a^3}$$

$$a^3 = \frac{2(39.102 \cancel{\text{ g}} \cancel{\text{ mol}^{-1}})}{(6.022 \times 10^{23} \cancel{\text{ mol}^{-1}})(0.856 \cancel{\text{ g}} \text{ cm}^{-3})}$$

$$a = 5.333\,408\,111 \times 10^{-8} \text{ cm}$$

$$a = 533.340\,811\,1 \text{ pm}$$

$$\boxed{a = 533.3 \text{ pm}}$$

Then from the equation

$$d_{hkl} = \frac{1}{(h^2 + k^2 + l^2)^{1/2}} = \frac{533.340\,811\,1\text{ pm}}{(h^2 + k^2 + l^2)^{1/2}}$$

$$\text{For (200) planes, } d_{200} = \frac{533.340\,811\,1\text{ pm}}{\sqrt{4}} = 266.670\,405\,6\text{ pm}$$

$$\boxed{d_{200} = 266.7\text{ pm}}$$

$$\text{For (110) planes, } d_{110} = \frac{533.340\,811\,1\text{ pm}}{\sqrt{2}} = 377.128\,904\,2\text{ pm}$$

$$\boxed{d_{110} = 377.1\text{ pm}}$$

$$\text{For (222) planes, } d_{222} = \frac{533.340\,811\,1\text{ pm}}{\sqrt{12}} = 153.962\,230\,4\text{ pm}$$

$$\boxed{d_{222} = 154.0\text{ pm}}$$

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**16.32.** Low-angle lines in the Cu  $K_\alpha$  powder pattern of KCl are found to be at  $\theta = 14.18^\circ$ ,  $20.25^\circ$ , and  $25.10^\circ$ . Find the crystal type from these data. (For Cu  $K_\alpha$   $\lambda = 154.18$  pm.) What other information is needed for a definitive determination?

**Solution:**

Given: pH 7,  $\partial E/\partial T = 2.18 \times 10^{-5}$  V K $^{-1}$

Required: see above

First, determine the  $d$  values for the three lines and take their ratios:

$$2d_1 = \frac{\lambda}{\sin(14.18)} \quad 2d_2 = \frac{\lambda}{\sin(20.25)} \quad 2d_3 = \frac{\lambda}{\sin(25.10)}$$

$$d_1 : d_2 : d_3 = \frac{1}{\sin(14.18)} : \frac{1}{\sin(20.25)} : \frac{1}{\sin(25.10)}$$

$$d_1 : d_2 : d_3 = 4.082\,149\,659 : 2.889\,195\,951 : 2.357\,381\,803$$

$$d_1 : d_2 : d_3 = 1 : 0.707\,763\,358 : 0.577485393$$

From Problem 16.16, for the cubic lattice,

$$d_{100} = a$$

$$d_{110} = \frac{\sqrt{2}a}{2} = 0.707$$

$$d_{111} = \frac{\sqrt{3}a}{3} = 0.5773$$

The ratios thus correspond to the cubic structure. To confirm the structure, if K $^+$  and Cl $^-$  reflect equally  $d = a/2$ , the theoretical density could be compared to the experimental value.

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**16.33.** The smallest observed diffraction angle of silver taken with Cu  $K_\alpha$  radiation ( $\lambda = 154.18$  pm) is  $19.176^\circ$ . This angle is associated with the (111) plane in the cubic close-packed structure of silver.

a. Determine the value of the unit cell length  $a$ .

b. If  $D(\text{Ag}) = 10.500 \text{ g cm}^{-3}$  and  $M = 107.87 \text{ g mol}^{-1}$ , calculate the number of atoms in the unit cell.

**Solution:**

Given: see above

Required: value of the unit cell length, number of atoms in the unit cell

$$\text{a. } d_{111} = \frac{\lambda}{2 \sin \theta} = \frac{154.18 \text{ pm}}{2 \sin(19.076)} = 235.877 \ 596 \ 9 \text{ pm}$$

$$\frac{a}{(h^2 + k^2 + l^2)^{1/2}} = 235.877 \ 596 \ 9 \text{ pm}$$

$$\frac{a}{(1^2 + 1^2 + 1^2)^{1/2}} = 235.877 \ 596 \ 9 \text{ pm}$$

$$a = 408.551 \ 982 \ 2 \text{ pm}$$

$$\boxed{a = 408.6 \text{ pm}}$$

b. The effective volume of each Ag atom is

$$V_{\text{Ag}} = \frac{M}{DN_{\text{av}}} = \frac{107.87 \text{ g mol}^{-1}}{(10.500 \text{ g m}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$V_{\text{Ag}} = 1.705 \ 967 \ 01 \times 10^{-23} \text{ cm}^3$$

$$V_{\text{Ag}} = 1.705 \ 967 \ 01 \times 10^7 \text{ pm}^3$$

$$V_{\text{cell}} = a^3 = (408.6 \text{ pm})^3 = 6.821 \ 738 \ 806 \times 10^7 \text{ pm}^3$$



The number of atoms per unit cell is

$$N = \frac{V_{\text{cell}}}{V_{\text{Ag}}} = \frac{6.821\,738\,806 \times 10^7 \text{ pm}^3}{1.705\,967\,01 \times 10^7 \text{ pm}^3} = 3.998\,751\,89$$

$$N = 4$$

This is an indication that Ag is fcc.

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**16.34.** Sodium fluoride is known to form a cubic closed-packed structure. The smallest angle obtained with Cu  $K_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) is  $16.72^\circ$  and is derived from the (111) planes. Find the value of  $a$ , the unit cell parameter.

**Solution:**

Given: see above

Required: the unit cell parameter

$$d_{111} = \frac{\lambda}{2 \sin \theta} = \frac{154.2 \text{ pm}}{2 \sin(16.72)}$$

$$d_{111} = 267.992 \text{ 288 4 pm}$$

$$d_{111} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} = \frac{a}{\sqrt{3}}$$

$$267.992 \text{ 288 4 pm} = \frac{a}{\sqrt{3}}$$

$$a = 464.176 \text{ 259 6 pm}$$

$$\boxed{a = 464.2 \text{ pm}}$$

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**16.35.** The X-ray powder pattern of NaCl is taken with a chromium tube giving  $\text{Cr } K_{\alpha} = 229.1 \text{ pm}$ . The  $\theta$  values of the lines are:  $20^{\circ}36'$ ,  $23^{\circ}58'$ ,  $35^{\circ}4'$ ,  $42^{\circ}21'$ ,  $44^{\circ}43'$ ,  $54^{\circ}20'$ ,  $62^{\circ}17'$ ,  $65^{\circ}16'$ . From these data determine the value of each  $d_{hkl}$  and index the lines. From the  $hkl$  values, show that this is a face-centered system.

**Solution:**

Given: above data

Required: see above

First, calculate decimal equivalent of  $\theta$  values and the  $\sin \theta$ . From each value of  $\theta$ , calculate the value of  $d_{hkl} = \frac{\lambda}{2 \sin \theta}$ .

$\theta$		$\sin \theta$	$d_{hkl} = \frac{229.1 \text{ pm}}{2 \sin \theta}$	$h \ k \ l$	$a$
$20^{\circ}36'$	20.600	0.351 841 648	325.572 599 6	1 1 1	564.0
$23^{\circ}58'$	23.967	0.406 210 411	281.996 711 3	2 0 0	564.0
$35^{\circ}4'$	35.067	0.574 533 936	199.378 997 2	2 2 0	564.0
$42^{\circ}21'$	42.350	0.673 657 707	170.041 845 9	3 1 1	563.8
$44^{\circ}43'$	44.717	0.703 605 57	162.804 282 5	2 2 2	564.0
$54^{\circ}20'$	54.333	0.812 419 487	140.998 587 3	4 0 0	564.0
$62^{\circ}17'$	62.283	0.885 255 665	129.397 647	3 3 1	564.0
$65^{\circ}16'$	65.267	0.908 267 352	126.119 253	4 2 0	563.9

Ignore the final two columns for the time being.  
Assume that NaCl has a cubic crystal structure.

Then

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$$

If we index the first three angles obtained from NaCl according to the (100), (110), (111) planes of the simple cubic lattice, the value of  $a$  should be the same in each case.

$$a = d_{hkl} \sqrt{1^2 + 0 + 0} = 325.572\,599\,6\,\text{pm}(\sqrt{1}) = 325.572\,599\,6\,\text{pm}$$

$$a = d_{hkl} \sqrt{1^2 + 1^2 + 0} = 281.996\,711\,3\,\text{pm}(\sqrt{2}) = 398.803\,573\,7\,\text{pm}$$

$$a = d_{hkl} \sqrt{1^2 + 1^2 + 1^2} = 199.378\,997\,2\,\text{pm}(\sqrt{3}) = 345.334\,553\,1\,\text{pm}$$

Since the unit cell dimension  $a$  is not the same, this does not allow indexing as a simple cubic system.

An attempt to index the first line with  $d_{110}$  gives

$$a = 325.572\,599\,6\,\text{pm}(\sqrt{1^2 + 1^2 + 0}) = 460.429\,185\,9\,\text{pm}$$

And the next set of  $hkl$  values must give the value

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{460.429\,185\,9\,\cancel{\text{pm}}}{281.996\,711\,3\,\cancel{\text{pm}}} = 1.632\,746\,651$$

No set of integers will give this value.

If the first line is indexed as 111, we have

$$a = 325.572\,599\,6\,\text{pm}(\sqrt{1^2 + 1^2 + 1^2}) = 563.908\,284\,1\,\text{pm}$$

And, as in the last case, the next line must be indexed such that

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{563.908\,284\,1\,\cancel{\text{pm}}}{281.996\,711\,3\,\cancel{\text{pm}}} = 1.999\,698\,087 = 2$$

This allows  $h$ ,  $k$ , or  $l = 2$  corresponding to planes (200), (020), (002).

The rest of the planes can be indexes as listed in the final columns of the table with the corresponding values of  $a$ . These correspond to the lines expected for an fcc structure as listed in Figure 16.20.

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**16.36.** Cadmium sulfide has been used as a yellow pigment by artists. The sulfide crystallizes with cadmium occupying  $\frac{1}{2}$  of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of cadmium sulfide?

**Solution:**

Given: see above

Required: formula of cadmium sulfide

In a closest-packed array there are two tetrahedral holes for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

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**16.37.** Rutile is a mineral that contains titanium and oxygen. The structure of rutile may be described as a closest-packed array of oxygen atoms with titanium in  $\frac{1}{2}$  of the octahedral holes. What is the formula of rutile? What is the oxidation number of titanium?

**Solution:**

Given: see above

Required: formula of rutile, the oxidation number of titanium

In a closest-packed array, there is one octahedral hole for each anion. If only half of the octahedral holes are occupied by titanium atoms, there are twice as many oxygen atoms as titanium ions, and the formula as  $\text{TiO}_2$ . With each oxygen as -2, the titanium must be +4.

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Then the maximum radius of the circle representing the void can be no more than  $AV - R$ , that is,

$$\frac{AG}{AV} = \frac{R}{R+r} = \sqrt{\frac{2}{3}}$$

$$r = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} R = 0.224\,744\,871R$$

$$\boxed{r = 0.225R}$$

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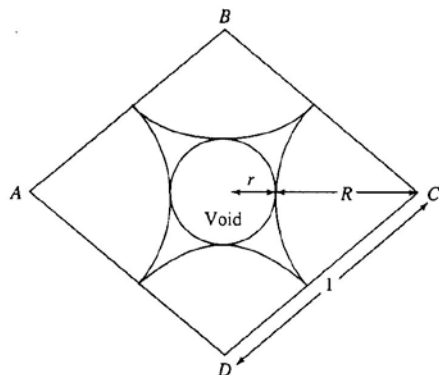
**16.39.** An octahedral hole is surrounded by six spheres of radius  $R$  in contact. If one-sixth of each of the six coordinating spheres contributes to the volume of the octahedron surrounding the hole, calculate the maximum radius of the sphere that can be accommodated.

**Solution:**

Given: see above

Required: maximum radius

Take a section through an octahedron with sides of unit length:



The diagonal  $AC$  is  $\sqrt{2}$ .

From the isosceles right triangle,

$$\frac{AC}{AB} = \frac{\sqrt{2}}{1}$$

If  $r$  is the radius of the void, then

$$\frac{2R + 2r}{2R} = \frac{\sqrt{2}}{1}$$

$$r = \sqrt{2}R - R = 0.414\ 213\ 562R$$

$$\boxed{r = 0.414R}$$

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**16.40.** Calculate the value of  $\Delta E_c$  of the RbBr from the following information:  $\Delta_f H = -414 \text{ kJ mol}^{-1}$ ;  $I$  (ionization energy, Rb) =  $397 \text{ kJ mol}^{-1}$ ;  $\Delta_{\text{sub}} H(\text{Rb}) = 84 \text{ kJ mol}^{-1}$ ;  $D_0(\text{Br}_2) = 192 \text{ kJ mol}^{-1}$ ;  $A$  (electron affinity, Br) =  $318 \text{ kJ mol}^{-1}$ .

**Solution:**

Given: above data

Required: value of  $\Delta E_c$

From Eq. 16.58,

$$\Delta E_c = -\Delta_f H + \Delta_{\text{sub}} H + \frac{1}{2} D_0 + I - A$$

$$\Delta E_c = \left[ 414 + 84 + \frac{1}{2}(192) + 397 - 318 \right] \text{ kJ mol}^{-1}$$

$$\boxed{\Delta E_c = 673 \text{ kJ mol}^{-1}}$$

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**16.41.** Some of the  $d$  spacings for the mineral canfieldite ( $\text{Ag}_8\text{SnS}_6$ ) are 3.23, 3.09, 3.04, 2.81, and 2.74 Å obtained with Cu  $K_\alpha$  X rays ( $\lambda = 1.5418$  Å).

a. Find the corresponding angles of diffraction.

b. This is a cubic system with  $a = 21.54$  Å; determine the  $hkl$  values for the first 3  $d$  spacings.

**Solution:**

Given: see above

Required: angles of diffraction,  $hkl$  values

a.  $n \lambda = 2d \sin \theta$

$d/\text{pm}$	323	309	304	284	274
$\theta$	$13.81^\circ$	$14.45^\circ$	$14.69^\circ$	$15.75^\circ$	$16.33^\circ$

b.  $\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$

For  $d = 323$  pm:

$$\frac{1}{d^2} = \frac{1}{(323 \text{ pm})^2} = \frac{h^2 + k^2 + l^2}{(21.54 \text{ \AA} \times 10^2 \text{ pm } \text{\AA}^{-1})^2}$$

$$h^2 + k^2 + l^2 = 44.471 \ 968 \ 48$$

$$6^2 + 2^2 + 2^2 = 36 + 4 + 4 = 44$$

For  $d = 309$  pm:

$$\frac{1}{d^2} = \frac{1}{(309 \text{ pm})^2} = \frac{h^2 + k^2 + l^2}{(21.54 \text{ \AA} \times 10^2 \text{ pm } \text{\AA}^{-1})^2}$$

$$h^2 + k^2 + l^2 = 48.593 \ 081 \ 35$$

$$4^2 + 4^2 + 4^2 = 48$$

For  $d = 304$  pm

$$\frac{1}{d^2} = \frac{1}{(304 \text{ pm})^2} = \frac{h^2 + k^2 + l^2}{(21.54 \text{ \AA} \times 10^2 \text{ pm } \text{\AA}^{-1})^2}$$

$$h^2 + k^2 + l^2 = 50.204 \ 683 \ 17$$

$$5^2 + 4^2 + 3^2 = 50$$

Note that other combinations of  $hkl$  values are possible, as well as different orders of the values given. As higher values of  $hkl$  are used, more possibilities exist, making it more difficult to decide on the correct values. Help in this task is provided by knowledge of the lines that are forbidden for the particular crystal type, and of the extinction caused by absorption by different atoms in the crystal layers.

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**16.42.** A copper selenide mineral ( $\text{Cu}_5\text{Se}_4$ ) called athabascaite is orthorhombic with  $a = 8.277$ ,  $b = 11.982$ ,  $c = 6.441$  Å. Strong intensity lines using Cu  $K_\alpha$  X rays ( $\lambda = 154.18$  pm) are observed at  $12.95^\circ$ ,  $13.76^\circ$ , and  $14.79^\circ$ . Determine the  $d$  spacings and assign  $hkl$  values to these lines.

**Solution:**

Given: see above

Required:  $d$  spacings, assign  $hkl$  values

$$n\lambda = 2d \sin \theta$$

$$d_{12.95^\circ} = 344 \text{ pm}; d_{13.76^\circ} = 324 \text{ pm}; d_{14.79^\circ} = 302 \text{ pm}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

With the values given,

$$\frac{1}{(d/\text{pm})^2} = \frac{h^2}{822.7^2} + \frac{k^2}{1198.2^2} + \frac{l^2}{644.1^2}$$

$$\frac{1}{d^2} = \frac{h^2}{676\,835.29} + \frac{k^2}{1435\,683.24} + \frac{l^2}{414\,864.81}$$

With  $d = 344$  pm, agreement is obtained with  $h = 2$ ,  $k = 0$ , and  $l = 1$ :

$$\text{LHS} = \frac{1}{344^2} = 8.450\,513\,791 \times 10^{-6}$$

$$\text{RHS} = \frac{2^2}{822.7^2} + \frac{0^2}{1198.2^2} + \frac{1^2}{644.1^2}$$

$$\text{RHS} = 5.909\,857\,33 \times 10^{-6} + 0 + 2.410\,423\,772 \times 10^{-6}$$

$$\text{RHS} = 8.320\,281\,102 \times 10^{-6}$$

With  $d = 324$  pm, agreement is obtained with  $h = 0$ ,  $k = 0$ , and  $l = 2$ :

$$\text{LHS} = \frac{1}{324^2} = 9.525\,986\,892 \times 10^{-6}$$

$$\text{RHS} = 0 + 0 + \frac{2^2}{644.1^2}$$

$$\text{RHS} = 9.641\,695\,086 \times 10^{-6}$$

With  $d = 302$  pm, agreement is obtained with  $h = 0$ ,  $k = 4$ , and  $l = 0$ :

$$\text{LHS} = \frac{1}{302^2} = 10.964\,431\,38 \times 10^{-6}$$

$$\text{RHS} = 0 + \frac{4^2}{1198.2^2} + 0$$

$$\text{RHS} = 11.144\,519\,59 \times 10^{-6}$$

In the latter case, agreement is obtained with  $h = 1$ ,  $k = 0$ , and  $l = 2$  ( $\text{RHS} = 11.0 \times 10^{-6}$ ), but in view of the crystal type (040) is more likely.

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**\*16.43.** Zinc blende is the face-centered cubic form of ZnS with Zn at  $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2};$

$\frac{1}{2}, \frac{1}{2}, 0$  and with S at  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}.$

- Determine the structure factor from the (111) planes that gives rise to the lowest angle reflection at  $\theta = 14.30^\circ$  using Cu  $K_\alpha$  ( $\lambda = 154.18$  pm).
- Calculate the dimension  $a$  of the unit cell.

**Solution:**

Given: see above

Required: structure factor, dimension  $a$  of the unit cell

- From Eq. 16.38,

$$F(hkl) = \sum_{j=1}^N f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

$$\begin{aligned} F(hkl) = f_{\text{Zn}} & \left[ \exp 2\pi i(0) + \exp 2\pi i\left(\frac{1}{2} + \frac{1}{2}\right) + \exp 2\pi i\left(\frac{1}{2} + \frac{1}{2}\right) + \exp 2\pi i\left(\frac{1}{2} + \frac{1}{2}\right) \right] \\ & + \left[ f_{\text{S}} \exp 2\pi i\left(\frac{1}{4} + \frac{1}{4} + \frac{1}{4}\right) + \exp 2\pi i\left(\frac{1}{4} + \frac{3}{4} + \frac{3}{4}\right) + \exp 2\pi i\left(\frac{3}{4} + \frac{1}{4} + \frac{3}{4}\right) \right. \\ & \left. + \exp 2\pi i\left(\frac{3}{4} + \frac{3}{4} + \frac{1}{4}\right) \right] F(hkl) \end{aligned}$$

$$F(hkl) = f_{\text{Zn}} [1 + 3\exp(2\pi i)] + f_{\text{S}} \left[ \exp\left(\frac{3\pi i}{2}\right) + 3\exp\left(\frac{7\pi i}{2}\right) \right]$$

$$\boxed{F(hkl) = 4f_{\text{Zn}} - 4if_{\text{S}}}$$

$$a = \frac{\lambda}{2 \sin \theta} (h^2 + k^2 + l^2)^{1/2}$$

**b.** 
$$a = \frac{154.18 \text{ pm} \times \sqrt{3}}{2(0.247)}$$

$$a = 540.582 \text{ 173 1 pm}$$

$$\boxed{a = 540.6 \text{ pm}}$$

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**16.44.** Calculate the Debye temperature of tungsten that is isotropic (an assumption of the Debye model). The cutoff frequency is given by

$$\nu_D = \left( \frac{9N}{4\pi V} \right)^{1/3} \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)^{-1/3}$$

where

$$c_l = 5.2496 \times 10^5 \text{ cm s}^{-1}$$

and

$$c_t = 2.9092 \times 10^5 \text{ cm s}^{-1}$$

are the longitudinal and trasverse elastic wave velocities, respectively, in tungsten.

**Solution:**

Given: see above

Required: Debye temperature of tungsten

The number of atoms per unit volume must be calculated

$$\frac{N}{V} = \frac{N_{\text{av}} D}{A}$$

Where  $A$  is the atomic mass,  $D$  is the density, and  $N_{\text{av}}$  is the Avogadro's number.

$$\nu_D = \left( \frac{9N}{4\pi V} \right)^{1/3} \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)^{-1/3}$$

$$\nu_D = \left[ \frac{9 \left( 19.271 \text{ g cm}^{-3} \right) \left( 6.022 \times 10^{23} \text{ mol}^{-1} \right)}{4\pi \left( 183.85 \text{ g mol}^{-1} \right)} \right]^{1/3} \times \left[ \frac{1}{\left( 5.2496 \times 10^5 \text{ cm s}^{-1} \right)^3} + \frac{2}{\left( 2.9092 \times 10^5 \text{ cm s}^{-1} \right)^3} \right]^{-1/3}$$

$$\nu_D = 8.004\,707\,251 \times 10^{12} \text{ s}^{-1}$$

$$\text{Then } \Theta_D = \frac{h\nu_D}{k_B} = \frac{(6.6262 \times 10^{-34} \text{ J s})(8.004\,707\,251 \times 10^{12} \text{ s}^{-1})}{(1.3807 \times 10^{-23} \text{ J K}^{-1})}$$

$$\Theta_D = 384.1586962 \text{ K}$$

$$\boxed{\Theta_D = 384 \text{ K}}$$

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CHAPTER

# 17

The Liquid State

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## Physical Chemistry

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# Problems and Solutions

## Chapter 17

### Thermodynamic Properties of Liquids

**17.1.** The density of liquid ethanol at 20 °C is  $0.790 \text{ g cm}^{-3}$ , and the van der Waals constant  $a$  is  $1.218 \text{ Pa m}^6 \text{ mol}^{-2}$ . Estimate the internal pressure and the potential-energy contribution to the internal energy.

[Solution](#)

**17.2.** In Example 17.3 (page 905), we obtained the internal pressure of liquid water from the van der Waals constant  $a$ . A more reliable value is obtained by use of Eq. 17.2, from the *thermal pressure coefficient*  $(\partial P/\partial T)_V$ ; this quantity is the ratio  $\alpha/\kappa$  of the coefficient of expansion  $\alpha[(1/V)(\partial V/\partial T)_P]$  to the compressibility  $\kappa[-(1/V)(\partial V/\partial P)_T]$ . For water at 1 bar pressure and 298 K the thermal pressure coefficient is  $6.60 \times 10^6 \text{ Pa K}^{-1}$ . Calculate the internal pressure.

[Solution](#)

**17.3.** The density of liquid benzene at 0 °C is  $0.899 \text{ g cm}^{-3}$ , and the van der Waals constant  $a$  is  $1.824 \text{ m}^6 \text{ mol}^{-2} \text{ Pa}$ . Estimate the internal pressure and the potential-energy contribution to the internal energy.

[Solution](#)

**17.4.** Make a better estimate of the internal energy of liquid benzene from its thermal pressure coefficient  $(\partial P/\partial T)_V$ , which at 298 K and 1 bar pressure is  $1.24 \times 10^6 \text{ Pa K}^{-1}$ .

[Solution](#)

**17.5.** Calculate the internal pressures of the following liquids at 298 K and 1 bar pressure from their thermal pressure coefficients, which are as follows:

Hg:	$4.49 \times 10^6 \text{ Pa K}^{-1}$
<i>n</i> -Heptane:	$8.53 \times 10^5 \text{ Pa K}^{-1}$
<i>n</i> -Octane:	$1.01 \times 10^6 \text{ Pa K}^{-1}$
Diethyl ether:	$8.06 \times 10^5 \text{ Pa K}^{-1}$

[Solution](#)

- 17.6.** The thermal pressure coefficient  $(\partial P/\partial T)_V$ , for  $\text{CCl}_4$  vapor at 298 K and 10 Pa pressure, is  $115 \text{ Pa K}^{-1}$ . That for liquid  $\text{CCl}_4$  at 298 K and 1 bar pressure is  $1.24 \times 10^6 \text{ Pa K}^{-1}$ . Calculate the internal pressures of the vapor and the liquid under these conditions.

[Solution](#)

- \*17.7.** The following data apply to liquid acetic acid at 1 atm pressure and 293 K: density,  $d = 1.049 \text{ g cm}^{-3}$ ; coefficient of expansion,  $\alpha = 1.06 \times 10^{-3} \text{ K}^{-1}$ ; compressibility,  $\kappa = 9.08 \times 10^{-10} \text{ Pa}^{-1}$ ; van der Waals constant,  $a = 1.78 \text{ m}^6 \text{ Pa mol}^{-2}$ . Make two estimates of the internal pressure  $P_i$ , (a) using  $\alpha$  and  $\kappa$  and (b) using  $a$ .

[Solution](#)

- \*17.8. a.** Derive the relationship

$$C_P - C_V = \frac{\alpha^2 VT}{\kappa}$$

where  $\alpha$  is the coefficient of expansion and  $\kappa$  is the compressibility.

- b.** The value of  $C_{V,m}$  for liquid  $\text{CCl}_4$  at 298 K and at 1 bar pressure is  $89.5 \text{ J K}^{-1} \text{ mol}^{-1}$ . Obtain the value of  $C_{P,m}$  using the following data:  $V_m = 97 \text{ cm}^3 \text{ mol}^{-1}$ ;  $\alpha = 1.24 \times 10^{-3} \text{ K}^{-1}$ ;  $\kappa = 10.6 \times 10^{-5} \text{ bar}^{-1}$ .

- c.** Calculate  $C_{P,m} - C_{V,m}$  for liquid acetic acid using the data given in Problem 17.7.

[Solution](#)

### Intermolecular Energies

- 17.9.** A liquid having a molar volume of  $50 \text{ cm}^3$  is converted into a vapor having a molar volume of  $50 \text{ dm}^3$ . By what factor does the average intermolecular energy change?

[Solution](#)

- 17.10.** Calculate the maximum energy of attraction, in J and in  $\text{kJ mol}^{-1}$ , when a  $\text{Ca}^{2+}$  ion is separated from a molecule of dipole moment  $6.18 \times 10^{-30} \text{ C m}$  ( $= 1.85 \text{ D}$ ; this is the dipole moment of water) by a distance of 500 pm in a vacuum.

[Solution](#)

**17.11.** Calculate the energy of attraction, in J and in  $\text{kJ mol}^{-1}$ , when a  $\text{Ca}^{2+}$  ion is separated in a vacuum from a  $\text{Cl}^-$  ion by a distance of 500 pm.

[Solution](#)

**17.12.** Calculate the energy of attraction, in J and in  $\text{kJ mol}^{-1}$ , when a  $\text{Ca}^{2+}$  ion is separated in a vacuum by a distance of 500 pm, from a nonpolar molecule (having zero dipole moment) but a polarizability of  $2.0 \times 10^{-30} \text{ m}^3$ .

[Solution](#)

**17.13.** Calculate the average energy of attraction, in J and in  $\text{kJ mol}^{-1}$ , for two molecules of dipole moments  $6.18 \times 10^{-30} \text{ C m}$  separated in a vacuum at  $25^\circ\text{C}$  by a distance of 500 pm.

[Solution](#)

**17.14.** The following values for  $A$  and  $B$  in the Lennard-Jones 6–12 function (Eq. 17.21) have been given for  $\text{N}_2$ :

$$A = 1.34 \times 10^{-5} \text{ J pm}^6$$

$$B = 3.42 \times 10^{10} \text{ J pm}^{12}$$

Calculate the equilibrium separation  $r_0$  and the classical dissociation energy  $E_0$ , in J and in  $\text{J mol}^{-1}$ .

[Solution](#)

**\*17.15.** The following data apply to HBr: dipole moment,  $\mu = 2.60 \times 10^{-30} \text{ C m}$ ; polarizability,  $\alpha = 3.58 \times 10^{-30} \text{ m}^3$ ; oscillation frequency,  $\nu_0 = 3.22 \times 10^{15} \text{ s}^{-1}$ . Estimate the dipole-dipole, dipole-(induced dipole), and dispersion energies in J and in  $\text{kJ mol}^{-1}$  for two HBr molecules separated by 500 pm, at  $25^\circ\text{C}$ .

[Solution](#)



**\*17.16.** The following are the polarizabilities and oscillation frequencies for Ne, Ar, and Kr:

	Ne	Ar	Kr
Polarizability, $\alpha/10^{-30} \text{ m}^3$	0.396	1.63	2.48
Frequency, $\nu_0/10^{15} \text{ s}^{-1}$	5.21	3.39	2.94

Calculate the dispersion energies for Ne, Ar, and Kr corresponding to a separation of 500 pm. Related data for He and Xe are given in Table 17.3; plot the five calculated values against the boiling points of the noble gases:

	He	Ne	Ar	Kr	Xe
Boiling point, $T_b/\text{K}$	4.22	27.3	87.3	119.9	165.1

[Solution](#)

**\*17.17.** In Table 17.3 and Problem 17.16 the dispersion energies of noble gases were calculated for a constant interatomic distance of 500 pm. More realistic values are:

	He	Ne	Ar	Kr	Xe
Interatomic distances/pm	240	320	380	400	420

Recalculate the dispersion energies for these distances, and again plot the five values against the boiling points, which were given in Problem 17.16.

The experimental value for the enthalpy of vaporization of liquid argon is  $6.7 \text{ kJ mol}^{-1}$ . Make an estimate of the enthalpy of vaporization from your calculated value of  $E_p$  (at 380 pm), assuming the liquid to have a close-packed structure with each atom having 12 nearest neighbors.

[Solution](#)

- \*17.18.** Estimate the interaction energy between an argon atom and a water molecule at a separation of 600 pm, which is approximately the distance of closest approach. The necessary data are: H<sub>2</sub>O: dipole moment,  $\mu = 6.18 \times 10^{-30}$  C m; Ar: polarizability,  $\alpha = 1.63 \times 10^{-30}$  m<sup>3</sup>.

Argon forms a solid hydrate, Ar·5H<sub>2</sub>O, but the binding energy between Ar and H<sub>2</sub>O is about 40 kJ mol<sup>-1</sup>, which is a good deal larger than the energy calculated from the dipole moment and polarizability. Suggest a reason for this discrepancy.

[Solution](#)

- \*17.19. a.** The Lennard-Jones potential

$$E = -\frac{A}{r^6} + \frac{B}{r^n}$$

can be formulated in a different way by expressing  $A$  and  $B$  in terms of the minimum energy  $E_{\min}$  and the value  $r_0$  of  $r$  at the minimum energy. Obtain the expression for  $E$  in terms of  $E_{\min}$  and  $r_0$ .

**b.** If  $r^*$  is the value of  $r$  when  $E = 0$ , obtain the relationship between  $r^*$  and  $r_0$ .

**c.** The Lennard-Jones potential is often used with  $n = 12$ , and the equations are then simpler. Obtain  $E$  in terms of  $E_{\min}$  and  $r_0$  and in terms of  $E_{\min}$  and  $r^*$ , for this special case of  $n = 12$ .

[Solution](#)

### Essay Questions

- 17.20.** Explain qualitatively how intermolecular forces of attraction are related to the following properties of a liquid:

- a.** vapor pressure;
- b.** enthalpy of vaporization;
- c.** normal boiling point;
- d.** entropy of vaporization.

- 17.21.** Explain clearly the difference between dipole-dipole and London (dispersion) forces. With reference to a few examples, discuss the magnitudes of attractive energies arising from these forces.

**Solutions**

**17.1.** The density of liquid ethanol at 20 °C is  $0.790 \text{ g cm}^{-3}$ , and the van der Waals constant  $a$  is  $1.218 \text{ Pa m}^6 \text{ mol}^{-2}$ . Estimate the internal pressure and the potential-energy contribution to the internal energy.

**Solution:**

Given:  $T = 20 \text{ °C}$ ,  $\rho = 0.790 \text{ g cm}^{-3}$ ,  $a = 1.218 \text{ Pa m}^6 \text{ mol}^{-2}$

Required:  $P_i$ ,  $E_p$

The internal pressure where the van der Waals equation applies, is given by Eq. 17.4

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$$

Since we have the density of ethanol, we can calculate the molar volume using the molar mass of ethanol.

$$M_{\text{ethanol}} = (2 \times 12.011 + 6 \times 1.00794 + 15.9994) \text{ g mol}^{-1}$$

$$M_{\text{ethanol}} = 46.06904 \text{ g mol}^{-1}$$

$$V_m = \frac{M_{\text{ethanol}}}{\rho}$$

$$V_m = \frac{46.06904 \text{ g mol}^{-1}}{0.790 \text{ g cm}^{-3}}$$

$$V_m = 58.315\,240\,51 \cancel{\text{ cm}^3} \text{ mol}^{-1} \times 10^{-6} \frac{\text{ m}^3}{\cancel{\text{ cm}^3}}$$

$$V_m = 5.831\,524\,051 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Solving for  $P_i$  gives,

$$P_i = \frac{1.218 \text{ Pa m}^6 \text{ mol}^{-2}}{(5.831524051 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})^2}$$

$$P_i = 358165001.6 \text{ Pa}$$

$$\boxed{P_i = 3.58 \times 10^3 \text{ bar}}$$

From Eq. 17.9, we solve for  $E_p$

$$E_p = -\frac{a}{V_m}$$

$$E_p = -\frac{1.218 \text{ Pa m}^6 \text{ mol}^{-2}}{5.831524051 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

$$E_p = -20886.47821 \text{ Pa m}^3 \text{ mol}^{-1}$$

$$\boxed{E_p = -20.9 \text{ kJ mol}^{-1}}$$

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**17.2.** In Example 17.3 (page 905), we obtained the internal pressure of liquid water from the van der Waals constant  $a$ . A more reliable value is obtained by use of Eq. 17.2, from the *thermal pressure coefficient*  $(\partial P/\partial T)_V$ ; this quantity is the ratio  $\alpha/\kappa$  of the coefficient of expansion  $\alpha[(1/V)(\partial V/\partial T)_P]$  to the compressibility  $\kappa[-(1/V)(\partial V/\partial P)_T]$ . For water at 1 bar pressure and 298 K the thermal pressure coefficient is  $6.60 \times 10^6 \text{ Pa K}^{-1}$ . Calculate the internal pressure.

**Solution:**

Given:  $P = 1 \text{ bar}$ ,  $T = 298 \text{ K}$ ,  $\left(\frac{\partial P}{\partial T}\right)_V = 6.60 \times 10^6 \text{ Pa K}^{-1}$

Required:  $P_i$  from Eq. 17.2

The internal pressure given by Eq. 17.2 is

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

$$P_i = -100\,000 \text{ Pa} + 298 \text{ K} \left(6.60 \times 10^6 \text{ Pa K}^{-1}\right)$$

$$P_i = 1\,966\,700\,000 \text{ Pa}$$

$$P_i = 19\,667 \text{ bar}$$

$$\boxed{P_i = 19.7 \times 10^3 \text{ bar}}$$

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**17.3.** The density of liquid benzene at 0 °C is 0.899 g cm<sup>-3</sup>, and the van der Waals constant  $a$  is 1.824 m<sup>6</sup> mol<sup>-2</sup> Pa. Estimate the internal pressure and the potential-energy contribution to the internal energy.

**Solution:**

Given:  $T = 0\text{ °C}$ ,  $\rho = 0.899\text{ g cm}^{-3}$ ,  $a = 1.824\text{ Pa m}^6\text{ mol}^{-2}$

Required:  $P_i$ ,  $E_p$

We solve this problem using the same procedure as in problem 17.1.

The molar volume is calculated from the molar mass of benzene

$$M_{\text{benzene}} = (6 \times 12.011 + 6 \times 1.00794)\text{ g mol}^{-1}$$

$$M_{\text{benzene}} = 78.113\,64\text{ g mol}^{-1}$$

$$V_m = \frac{M_{\text{benzene}}}{\rho}$$

$$V_m = \frac{78.113\,64\text{ g mol}^{-1}}{0.899\text{ g cm}^{-3}}$$

$$V_m = 86.889\,477\,2\text{ cm}^3\text{ mol}^{-1} \times 10^{-6} \frac{\text{m}^3}{\text{cm}^3}$$

$$V_m = 8.688\,947\,72 \times 10^{-5}\text{ m}^3\text{ mol}^{-1}$$

Solving for  $P_i$  gives,

$$P_i = \frac{1.824\text{ Pa m}^6\text{ mol}^{-2}}{(8.688\,947\,72 \times 10^{-5}\text{ m}^3\text{ mol}^{-1})^2}$$

$$P_i = 241\,596\,403.9\text{ Pa}$$

$$\boxed{P_i = 2.42 \times 10^3\text{ bar}}$$

From Eq. 17.9, we solve for  $E_p$

$$E_p = -\frac{a}{V_m}$$

$$E_p = -\frac{1.824 \text{ Pa m}^6 \text{ mol}^{-2}}{8.688\,947\,72 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

$$E_p = -20\,992.185\,23 \text{ Pa m}^3 \text{ mol}^{-1}$$

$$E_p = -21.0 \text{ kJ mol}^{-1}$$

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**17.4.** Make a better estimate of the internal energy of liquid benzene from its thermal pressure coefficient  $(\partial P/\partial T)_V$ , which at 298 K and 1 bar pressure is  $1.24 \times 10^6 \text{ Pa K}^{-1}$ .

**Solution:**

Given:  $P = 1 \text{ bar}$ ,  $T = 298 \text{ K}$ ,  $\left(\frac{\partial P}{\partial T}\right)_V = 1.24 \times 10^6 \text{ Pa K}^{-1}$

Required:  $P_i$  from Eq. 17.2

We solve this problem using the same procedure as in problem 17.2.

The internal pressure given by Eq. 17.2 is

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

$$P_i = -100\,000 \text{ Pa} + 298 \text{ K} \left(1.24 \times 10^6 \text{ Pa K}^{-1}\right)$$

$$P_i = 369\,420\,000 \text{ Pa}$$

$$P_i = 3694.2 \text{ bar}$$

$$\boxed{P_i = 3.69 \times 10^3 \text{ bar}}$$

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**17.5.** Calculate the internal pressures of the following liquids at 298 K and 1 bar pressure from their thermal pressure coefficients, which are as follows:

Hg:	$4.49 \times 10^6 \text{ Pa K}^{-1}$
<i>n</i> -Heptane:	$8.53 \times 10^5 \text{ Pa K}^{-1}$
<i>n</i> -Octane:	$1.01 \times 10^6 \text{ Pa K}^{-1}$
Diethyl ether:	$8.06 \times 10^5 \text{ Pa K}^{-1}$

**Solution:**

Given:  $P = 1 \text{ bar}$ ,  $T = 298 \text{ K}$ ,  $\left(\frac{\partial P}{\partial T}\right)_V$  given above

Required:  $P_i$

We solve this problem using the same procedure as in problem 17.2.

The internal pressure given by Eq. 17.2 is

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

$$P_i = -100\,000 \text{ Pa} + 298 \text{ K} \left(4.49 \times 10^6 \text{ Pa K}^{-1}\right)$$

$$P_i = 1\,337\,920\,000 \text{ Pa}$$

$$P_i = 13\,379.2 \text{ bar}$$

a.  $P_i = 1.34 \times 10^4 \text{ bar}$

Repeating the same procedure as above, we obtain the following results:

b.  $P_i = 2.54 \times 10^3 \text{ bar}$

c.  $P_i = 3.01 \times 10^3 \text{ bar}$

d.  $P_i = 2.40 \times 10^3 \text{ bar}$

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**17.6.** The thermal pressure coefficient  $(\partial P/\partial T)_V$ , for  $\text{CCl}_4$  vapor at 298 K and 10 Pa pressure, is  $115 \text{ Pa K}^{-1}$ . That for liquid  $\text{CCl}_4$  at 298 K and 1 bar pressure is  $1.24 \times 10^6 \text{ Pa K}^{-1}$ . Calculate the internal pressures of the vapor and the liquid under these conditions.

**Solution:**

Given:  $T = 298 \text{ K}$ ,  $P_{\text{vapor}} = 10 \text{ Pa}$ ,  $\left(\frac{\partial P}{\partial T}\right)_{V, \text{vapor}} = 115 \text{ Pa K}^{-1}$ ,

$$P_{\text{liquid}} = 1 \text{ bar}, \left(\frac{\partial P}{\partial T}\right)_{V, \text{liquid}} = 1.24 \times 10^6 \text{ Pa K}^{-1}$$

Required:  $P_i$  for vapor and liquid

We solve this problem using the same procedure as in problem 17.2.

The internal pressure given by Eq. 17.2 is

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V$$

$$P_{i, \text{vapor}} = -10 \text{ Pa} + 298 \text{ K} (115 \text{ Pa K}^{-1})$$

$$P_{i, \text{vapor}} = 34\,260 \text{ Pa}$$

$$P_{i, \text{vapor}} = 0.342\,60 \text{ bar}$$

$$\boxed{P_{i, \text{vapor}} = 0.343 \text{ bar}}$$

For the liquid,

$$P_{i, \text{liquid}} = -100\,000 \text{ Pa} + 298 \text{ K} (1.24 \times 10^6 \text{ Pa K}^{-1})$$

$$P_{i, \text{liquid}} = 369\,420\,000 \text{ Pa}$$

$$P_{i, \text{liquid}} = 3694.2 \text{ bar}$$

$$\boxed{P_{i, \text{liquid}} = 3.69 \times 10^3 \text{ bar}}$$

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**\*17.7.** The following data apply to liquid acetic acid at 1 atm pressure and 293 K: density,  $d = 1.049 \text{ g cm}^{-3}$ ; coefficient of expansion,  $\alpha = 1.06 \times 10^{-3} \text{ K}^{-1}$ ; compressibility,  $\kappa = 9.08 \times 10^{-10} \text{ Pa}^{-1}$ ; van der Waals constant,  $a = 1.78 \text{ m}^6 \text{ Pa mol}^{-2}$ . Make two estimates of the internal pressure  $P_i$ , (a) using  $\alpha$  and  $\kappa$  and (b) using  $a$ .

**Solution:**

Given:  $P = 1 \text{ atm}$ ,  $T = 293 \text{ K}$ ,  $d = 1.049 \text{ g cm}^{-3}$ ,  $\alpha = 1.06 \times 10^{-3} \text{ K}^{-1}$ ,  $\kappa = 9.08 \times 10^{-10} \text{ Pa}^{-1}$

$$a_{\text{vdw}} = 1.78 \text{ m}^6 \text{ Pa mol}^{-2}$$

Required: a)  $P_i$  from  $\alpha$  and  $\kappa$  and

b)  $P_i$  from using  $a$

a. From Eq. 17.2, and knowing that the thermal pressure coefficient  $(\partial P / \partial T)_V$  is the ratio  $\alpha / \kappa$ ,

$$\left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{\partial P}{\partial T} \right)_V \text{ becomes } P_i = -P + T \left( \frac{\alpha}{\kappa} \right)$$

Solving for  $P_i$  we obtain,

$$P_i = -100\,000 \text{ Pa} + 293 \text{ K} \left( \frac{1.06 \times 10^{-3} \text{ K}^{-1}}{9.08 \times 10^{-10} \text{ Pa}^{-1}} \right)$$

$$P_i = 341\,948\,458.2 \text{ Pa}$$

$$P_i = 3419.484\,582 \text{ bar}$$

$$\boxed{P_i = 3.42 \times 10^3 \text{ bar}}$$

b. The internal pressure where the van der Waals equation applies, is given by Eq. 17.4

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{a}{V_m^2}$$

Using the density, we can calculate the molar volume using the molar mass of acetic acid.

$$M = (2 \times 12.011 + 4 \times 1.00794 + 2 \times 15.9994) \text{ g mol}^{-1}$$

$$M = 60.05256 \text{ g mol}^{-1}$$

$$V_m = \frac{M}{d}$$

$$V_m = \frac{60.05256 \text{ g mol}^{-1}}{1.049 \text{ g cm}^{-3}}$$

$$V_m = 57.247\,435\,65 \cancel{\text{ cm}^3} \text{ mol}^{-1} \times 10^{-6} \frac{\text{ m}^3}{\cancel{\text{ cm}^3}}$$

$$V_m = 5.724\,743\,565 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Solving for  $P_i$  gives,

$$P_i = \frac{1.78 \text{ Pa m}^6 \text{ mol}^{-2}}{(5.724\,743\,565 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})^2}$$

$$P_i = 543\,135\,171.5 \text{ Pa}$$

$$\boxed{P_i = 5.43 \times 10^3 \text{ bar}}$$

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**\*17.8. a.** Derive the relationship

$$C_p - C_v = \frac{\alpha^2 VT}{\kappa}$$

where  $\alpha$  is the coefficient of expansion and  $\kappa$  is the compressibility.

**b.** The value of  $C_{v,m}$  for liquid  $\text{CCl}_4$  at 298 K and at 1 bar pressure is  $89.5 \text{ J K}^{-1} \text{ mol}^{-1}$ . Obtain the value of  $C_{p,m}$  using the following data:  $V_m = 97 \text{ cm}^3 \text{ mol}^{-1}$ ;  $\alpha = 1.24 \times 10^{-3} \text{ K}^{-1}$ ;  $\kappa = 10.6 \times 10^{-5} \text{ bar}^{-1}$ .

**c.** Calculate  $C_{p,m} - C_{v,m}$  for liquid acetic acid using the data given in Problem 17.7.

**Solution:**

Given:  $T = 298 \text{ K}$ ,  $P = 1 \text{ bar}$ ,  $C_{v,m} = 89.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ,

$$V_m = 97 \text{ cm}^3 \text{ mol}^{-1}, \alpha = 1.24 \times 10^{-3} \text{ K}^{-1}, \kappa = 10.6 \times 10^{-5} \text{ bar}^{-1},$$

data from Problem 17.7

Required: see above

a. To derive the above relationship we start with Eq. 2.117 found in Chapter 2.

$$C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

Using one of the thermodynamic equations of state, Eq. 3.128,

$$\left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{\partial P}{\partial T} \right)_V$$

We make the following substitution:

$$C_p - C_v = \left[ \cancel{P} \cancel{P} + T \left( \frac{\partial P}{\partial T} \right)_V \right] \left( \frac{\partial V}{\partial T} \right)_P$$

$$C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

Using the definitions of the cubic expansion coefficient and the isothermal compressibility as defined by Eq. 3.139 and Eq. 142 we further solve,

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa \equiv \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

The expression first becomes,

$$C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V (V\alpha)$$

$$\frac{\alpha}{\kappa} = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \times V \left( \frac{\partial P}{\partial V} \right)_T$$

$$\frac{\alpha}{\kappa} = \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T$$

$$\frac{\alpha}{\kappa} = \left( \frac{\partial P}{\partial T} \right)_V$$

Thus,

$$C_p - C_v = T \frac{\alpha}{\kappa} (V\alpha)$$

$$\boxed{C_p - C_v = \frac{\alpha^2 VT}{\kappa}}$$

b. Using the expression above we can solve for  $C_{p,m}$ .

$$C_{P,m} = C_{V,m} + \frac{\alpha^2 V_m T}{\kappa}$$

$$C_{P,m} = 89.5 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{(1.24 \times 10^{-3} \text{ K}^{-1})^2 (97 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) (298 \text{ K})}{10.6 \times 10^{-5} \cancel{\text{bar}^{-1}} \times 10^{-5} \cancel{\text{bar}} \text{ Pa}^{-1}}$$

$$C_{P,m} = 131.430\,061\,9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{C_{P,m} = 131 \text{ J K}^{-1} \text{ mol}^{-1}}$$

c. From the data given in problem 17.7 we have,

$$V_m = 5.724\,743\,565 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}, P = 1 \text{ atm}, T = 293 \text{ K}, \alpha = 1.06 \times 10^{-3} \text{ K}^{-1}, \kappa = 9.08 \times 10^{-10} \text{ Pa}^{-1}$$

Therefore  $C_{P,m} - C_{V,m}$  is calculated as,

$$C_{P,m} - C_{V,m} = \frac{(1.06 \times 10^{-3} \text{ K}^{-1})^2 (5.724\,743\,565 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}) (293 \text{ K})}{9.08 \times 10^{-10} \text{ Pa}^{-1}}$$

$$C_{P,m} - C_{V,m} = 20.756\,280\,92 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{C_{P,m} - C_{V,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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**17.9.** A liquid having a molar volume of  $50 \text{ cm}^3$  is converted into a vapor having a molar volume of  $50 \text{ dm}^3$ . By what factor does the average intermolecular energy change?

**Solution:**

Given:  $V_{m,1} = 50 \text{ cm}^3$ ,  $V_{m,2} = 50 \text{ dm}^3$

Required: factor of intermolecular energy change

Since the intermolecular energy is inversely proportional to the sixth power of the intermolecular distance, it is inversely proportional to the square of the volume (Eq. 17.4,  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$ ). The volume has increased by a factor of  $10^3$ , and the energy therefore changes by a factor of  $10^{-6}$ .

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**17.10.** Calculate the maximum energy of attraction, in J and in kJ mol<sup>-1</sup>, when a Ca<sup>2+</sup> ion is separated from a molecule of dipole moment  $6.18 \times 10^{-30}$  C m (= 1.85 D; this is the dipole moment of water) by a distance of 500 pm in a vacuum.

**Solution:**

Given:  $\mu = 6.18 \times 10^{-30}$  C m,  $r = 500$  pm

Required:  $E_p$

We can calculate the maximum energy using Eq. 17.13,

$$E_p = \frac{z_A e \mu \cos \theta}{4\pi\epsilon_0\epsilon r^2}$$

For a separated species, this simplifies to

$$E_p = -\frac{z_A e \mu}{4\pi\epsilon_0 r^2} \text{ since } \cos \pi = -1$$

Solving, we obtain,

$$E_p = -\frac{(2)(1.602 \times 10^{-19} \text{ C})(6.18 \times 10^{-30} \text{ C m})}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(5.00 \times 10^{-10} \text{ m})^2}$$

$$E_p = -7.118\,550\,86 \times 10^{-20} \text{ N m}$$

$$\boxed{E_p = -7.12 \times 10^{-20} \text{ J}}$$

Converting to kJ per mole, we multiply by Avogadro's number and 10<sup>-3</sup>.

$$E_p = (-7.118\,550\,86 \times 10^{-20} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = -42\,867.913\,27 \text{ J mol}^{-1}$$

$$\boxed{E_p = -42.9 \text{ kJ mol}^{-1}}$$

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**17.11.** Calculate the energy of attraction, in J and in  $\text{kJ mol}^{-1}$ , when a  $\text{Ca}^{2+}$  ion is separated in a vacuum from a  $\text{Cl}^-$  ion by a distance of 500 pm.

**Solution:**

Given:  $r = 500 \text{ pm}$

Required:  $E_p$

We can calculate the maximum energy using Eq. 17.12,

$$E_p = \frac{z_A z_B e^2}{4\pi\epsilon_0\epsilon r}$$

$$E_p = \frac{(2)(-1)(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(5.00 \times 10^{-10} \text{ m})}$$

$$E_p = -9.226\,471\,26 \times 10^{-19} \text{ N m}^{-1}$$

$$\boxed{E_p = -9.23 \times 10^{-19} \text{ J}}$$

$$E_p = (-9.226\,471\,26 \times 10^{-19} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = -555\,618.099\,1 \text{ J mol}^{-1}$$

$$\boxed{E_p = -556 \text{ kJ mol}^{-1}}$$

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**17.12.** Calculate the energy of attraction, in J and in  $\text{kJ mol}^{-1}$ , when a  $\text{Ca}^{2+}$  ion is separated in a vacuum by a distance of 500 pm, from a nonpolar molecule (having zero dipole moment) but a polarizability of  $2.0 \times 10^{-30} \text{ m}^3$ .

Given:  $\alpha = 2.00 \times 10^{-30} \text{ m}^3$ ,  $r = 500 \text{ pm}$

Required:  $E_p$

In this case, we calculate the energy of attraction using Eq. 17.14,

$$E_p = -\frac{\alpha(z_A e)^2}{8\pi\epsilon_0\epsilon r^4}$$

Solving, we obtain,

$$E_p = -\frac{\alpha(z_A e)^2}{8\pi\epsilon_0\epsilon r^4}$$

$$E_p = -\frac{(2.00 \times 10^{-30} \text{ m}^3)(2 \times 1.602 \times 10^{-19} \text{ C})^2}{8\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(5.00 \times 10^{-10} \text{ m})^4}$$

$$E_p = -1.476\,235\,4 \times 10^{-20} \text{ N m}$$

$$\boxed{E_p = -1.48 \times 10^{-20} \text{ J}}$$

$$E_p = (-1.476\,235\,4 \times 10^{-20} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = -8889.889\,586 \text{ J mol}^{-1}$$

$$\boxed{E_p = -8.89 \text{ kJ mol}^{-1}}$$

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**17.13.** Calculate the average energy of attraction, in J and in  $\text{kJ mol}^{-1}$ , for two molecules of dipole moments  $6.18 \times 10^{-30} \text{ C m}$  separated in a vacuum at  $25^\circ\text{C}$  by a distance of 500 pm.

**Solution:**

Given:  $\mu = 6.18 \times 10^{-30} \text{ C m}$ ,  $T = 25^\circ\text{C}$ ,  $r = 500 \text{ pm}$

Required:  $E_p$

We solve for the average energy of attraction using Eq. 17.17.

$$E_p = -\frac{\mu_A^2 \mu_B^2}{24\pi^2 \epsilon_0^2 \epsilon^2 k_B T r^6}$$

$$E_p = -\frac{(6.18 \times 10^{-30} \text{ C m})^4}{24\pi^2 (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})^2 (1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})(5.00 \times 10^{-10} \text{ m})^6}$$

$$E_p = -1.22161 \times 10^{-21} \text{ J}$$

$$\boxed{E_p = -1.22 \times 10^{-21} \text{ J}}$$

$$E_p = (-1.22161 \times 10^{-21} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = -735.653542 \text{ J mol}^{-1}$$

$$\boxed{E_p = -0.736 \text{ kJ mol}^{-1}}$$

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**17.14.** The following values for  $A$  and  $B$  in the Lennard-Jones 6–12 function (Eq. 17.21) have been given for  $\text{N}_2$ :

$$A = 1.34 \times 10^{-5} \text{ J pm}^6$$

$$B = 3.42 \times 10^{10} \text{ J pm}^{12}$$

Calculate the equilibrium separation  $r_0$  and the classical dissociation energy  $E_0$ , in J and in  $\text{J mol}^{-1}$ .

**Solution:**

Given: Eq. 17.21,  $A = 1.34 \times 10^{-5} \text{ J pm}^6$ ,  $B = 3.42 \times 10^{10} \text{ J pm}^{12}$

Required:  $r_0$ ,  $E_0$

To solve for the equilibrium separation, we take the derivative of Eq. 17.21 and set it equal to zero. The resulting value of  $r$  corresponds to  $r_0$ .

$$E_p = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

$$\frac{dE_p}{dr} = \frac{6A}{r^7} - \frac{12B}{r^{13}} = 0$$

$$6Ar^6 = 12B$$

$$r_0 = \left( \frac{2B}{A} \right)^{1/6}$$

$$r_0 = \left( \frac{2 \times 3.42 \times 10^{10} \text{ J pm}^{12}}{1.34 \times 10^{-5} \text{ J pm}^6} \right)^{1/6}$$

$$r_0 = 414.946 \text{ 288 pm}$$

$$\boxed{r_0 = 415 \text{ pm}}$$

To solve for the energy at separation we use Eq. 17.21, substitution for the radius solved above.

$$E_0 = -\frac{A}{r_0^6} + \frac{B}{r_0^{12}}$$

$$E_0 = -\frac{1.34 \times 10^{-5} \text{ J pm}^6}{(414.946 \text{ 288 pm})^6} + \frac{3.42 \times 10^{10} \text{ J pm}^{12}}{(414.946 \text{ 288 pm})^{12}}$$

$$E_0 = -1.312 \text{ 573 1} \times 10^{-21} \text{ J}$$

$$\boxed{E_0 = -1.31 \times 10^{-21} \text{ J}}$$

Multiplying by Avogadro's number and  $10^{-3}$  we convert to kJ per mole.

$$E_0 = (-1.312 \text{ 573 1} \times 10^{-21} \text{ J})(6.022 \times 10^{23} \text{ mol})$$

$$E_0 = -790.431 \text{ 520 5 J mol}^{-1}$$

$$\boxed{E_0 = -0.790 \text{ kJ mol}^{-1}}$$

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**\*17.15.** The following data apply to HBr: dipole moment,  $\mu = 2.60 \times 10^{-30}$  C m; polarizability,  $\alpha = 3.58 \times 10^{-30}$  m<sup>3</sup>; oscillation frequency,  $\nu_0 = 3.22 \times 10^{15}$  s<sup>-1</sup>. Estimate the dipole-dipole, dipole-(induced dipole), and dispersion energies in J and in kJ mol<sup>-1</sup> for two HBr molecules separated by 500 pm, at 25 °C.

**Solution:**

Given:  $\mu = 2.60 \times 10^{-30}$  C m,  $\alpha = 3.58 \times 10^{-30}$  m<sup>3</sup>,  $\nu_0 = 3.22 \times 10^{15}$  s<sup>-1</sup>,  $r = 500$  pm,  $T = 25$  °C

Required: dipole-dipole energy, dipole-(induced dipole) energy, and dispersion energy

To determine the dipole-dipole energy for the two HBr molecules we use Eq. 17.17.

$$E_p = -\frac{\mu_A^2 \mu_B^2}{24\pi^2 \epsilon_0^2 \epsilon^2 k_B T r^6}$$

$$E_p = -\frac{(2.60 \times 10^{-30})^4}{24\pi^2 (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})^2 (1.381 \times 10^{-23} \text{ J K}^{-1} \times 298.15 \text{ K}) (5 \times 10^{-10} \text{ m})^6}$$

$$E_p = -3.825\,206\,2 \times 10^{-23} \text{ J}$$

$$\boxed{E_p = -3.83 \times 10^{-23} \text{ J}}$$

$$E_p = (-3.825\,206\,2 \times 10^{-23} \text{ J}) (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = -23.035\,391\,74 \text{ J mol}^{-1}$$

$$\boxed{E_p = -2.30 \times 10^{-2} \text{ kJ mol}^{-1}}$$

The dipole-(induced dipole) energy is given by Eq. 17.18.

$$E_p = -\frac{\alpha\mu^2}{2\pi\epsilon_0\epsilon r^6}$$

$$E_p = -\frac{(3.58 \times 10^{-30} \text{ m}^3)(2.60 \times 10^{-30} \text{ C m})^2}{2\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(5.00 \times 10^{-10} \text{ m})^6}$$

$$E_p = -2.78413513 \times 10^{-23} \text{ J}$$

$$\boxed{E_p = -2.78 \times 10^{-23} \text{ J}}$$

$$E_p = (-2.78413513 \times 10^{-23} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = -16.766606177 \text{ J mol}^{-1}$$

$$\boxed{E_p = -1.68 \times 10^{-2} \text{ kJ mol}^{-1}}$$

The potential energy due to the dispersion forces is given by Eq. 17.19.

$$E_p = -\frac{3h\nu_0\alpha^2}{4r^6}$$

$$E_p = -\frac{3(6.626 \times 10^{-34} \text{ J s})(3.22 \times 10^{15} \text{ s}^{-1})(3.58 \times 10^{-30})^2}{4(5.00 \times 10^{-10} \text{ m})^6}$$

$$E_p = -1.31254618 \times 10^{-21} \text{ J}$$

$$\boxed{E_p = -1.31 \times 10^{-21} \text{ J}}$$

$$E_p = (-1.31254618 \times 10^{-21} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = -790.4153124 \text{ J mol}^{-1}$$

$$\boxed{E_p = -0.790 \text{ kJ mol}^{-1}}$$

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**\*17.16.** The following are the polarizabilities and oscillation frequencies for Ne, Ar, and Kr:

	Ne	Ar	Kr
Polarizability, $\alpha/10^{-30} \text{ m}^3$	0.396	1.63	2.48
Frequency, $\nu_0/10^{15} \text{ s}^{-1}$	5.21	3.39	2.94

Calculate the dispersion energies for Ne, Ar, and Kr corresponding to a separation of 500 pm. Related data for He and Xe are given in Table 17.3; plot the five calculated values against the boiling points of the noble gases:

	He	Ne	Ar	Kr	Xe
Boiling point, $T_b/\text{K}$	4.22	27.3	87.3	119.9	165.1

**Solution:**

Given:  $\alpha$ ,  $\nu_0$ ,  $T_b$ ,  $r = 500 \text{ pm}$ , Table 17.3

Required:  $E_p$ , plot  $E_d$  against  $T_b$

Since we are given incomplete information for the frequency for He and Xe, we use Eq. 17.19 and the data found in Table 17.3 to solve for  $\nu_0$ .

$$v_0 = -\frac{4r^6 E_p}{3h\alpha^2}$$

For He

$$v_{0,\text{He}} = -\frac{4(500 \times 10^{-12} \text{ m})^6 (-4.6 \text{ J mol}^{-1})}{3(6.626 \times 10^{-34} \text{ J s})(0.20 \times 10^{-30} \text{ m}^3)^2}$$

$$v_{0,\text{He}} = 3.615\,806\,419 \times 10^{39} \text{ mol}^{-1} \text{ s}^{-1}$$

$$v_{0,\text{He}} = \frac{3.615\,806\,419 \times 10^{39} \cancel{\text{mol}^{-1}} \text{ s}^{-1}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}}$$

$$v_{0,\text{He}} = 6.004\,328\,162 \times 10^{15} \text{ s}^{-1}$$

For Xe

$$v_{0,\text{Xe}} = -\frac{4(500 \times 10^{-12} \text{ m})^6 (-850.0 \text{ J mol}^{-1})}{3(6.626 \times 10^{-34} \text{ J s})(4.00 \times 10^{-30} \text{ m}^3)^2}$$

$$v_{0,\text{Xe}} = 1.670\,345\,357 \times 10^{39} \text{ mol}^{-1} \text{ s}^{-1}$$

$$v_{0,\text{Xe}} = \frac{1.670\,345\,357 \times 10^{39} \cancel{\text{mol}^{-1}} \text{ s}^{-1}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}}$$

$$v_{0,\text{Xe}} = 2.773\,738\,553 \times 10^{15} \text{ s}^{-1}$$

$$E_p = -\frac{3h\nu_0\alpha^2}{4r^6}$$

$$E_p = -\frac{3(6.626 \times 10^{-34} \text{ J s})(\nu_0/\text{s}^{-1})(\alpha^2/\text{m}^3)^2}{4(500 \times 10^{-12} \text{ m})^6}$$

$$E_p = -3.180\,48 \times 10^{22} (\nu_0/\text{s}^{-1})(\alpha^2/\text{m}^3)^2$$

For He

$$E_p = -3.180\,48 \times 10^{22} (6.004\,328\,162 \times 10^{15})(0.20 \times 10^{-30})^2$$

$$E_p = -7.638\,658\,253 \times 10^{-24} \text{ J}; -4.6 \text{ J mol}^{-1}$$

For Xe

$$E_p = -3.180\,48 \times 10^{22} (2.773\,738\,553 \times 10^{15})(4.00 \times 10^{-30})^2$$

$$E_p = -1.411\,491\,199 \times 10^{-21} \text{ J}; -850 \text{ J mol}^{-1}$$

For Ar

$$E_p = -3.180\,48 \times 10^{22} (3.39 \times 10^{15})(1.63 \times 10^{-30})^2$$

$$E_p = -2.864\,623\,669 \times 10^{-22} \text{ J}; -172.507\,637\,3 \text{ J mol}^{-1}$$

For Ne

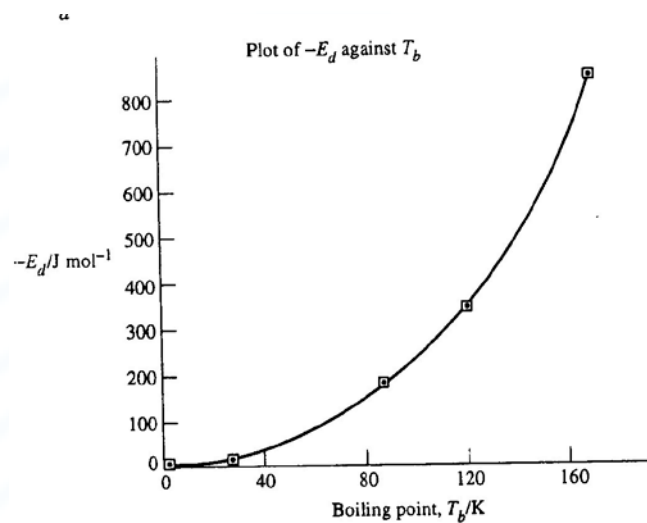
$$E_p = -3.180\,48 \times 10^{22} (5.21 \times 10^{15})(0.396 \times 10^{-30})^2$$

$$E_p = -2.598\,488\,29 \times 10^{-23} \text{ J}; -15.648\,096\,48 \text{ J mol}^{-1}$$

For Kr

$$E_p = -3.180\,48 \times 10^{22} (2.94 \times 10^{15})(2.48 \times 10^{-30})^2$$

$$E_p = -5.750\,999\,912 \times 10^{-22} \text{ J}; -346.325\,214\,7 \text{ J mol}^{-1}$$



Check  $E_p$  for He and Xe, directly taken from book or have to calculate it? Have the same values anyhow

[Back to Problem 17.16](#)

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**\*17.17.** In Table 17.3 and Problem 17.16 the dispersion energies of noble gases were calculated for a constant interatomic distance of 500 pm. More realistic values are:

	He	Ne	Ar	Kr	Xe
Interatomic distances/pm	240	320	380	400	420

Recalculate the dispersion energies for these distances, and again plot the five values against the boiling points, which were given in Problem 17.16.

The experimental value for the enthalpy of vaporization of liquid argon is  $6.7 \text{ kJ mol}^{-1}$ . Make an estimate of the enthalpy of vaporization from your calculated value of  $E_p$  (at 380 pm), assuming the liquid to have a close-packed structure with each atom having 12 nearest neighbors.

**Solution:**

Given: Table 17.3, Problem 17.16,  $r = 500 \text{ pm}$ ,

Required:  $E_d$ , plot  $E_d$  against  $T_b$

The values previously calculated (Problem 17.16) will be multiplied by the factor

$\left(\frac{500}{r/\text{pm}}\right)^6$  and then divided by the corresponding interatomic distances to the power of 6 according to the following equation

$$E_p = -\frac{3h\nu_0\alpha^2}{4r^6}$$

Sample calculation for He:

$$E_p = -7.638\,658\,253 \times 10^{-24} \text{ J}$$

$$\text{new } E_p = \left(-7.638\,658\,253 \times 10^{-24} \text{ J}\right) \left(\frac{500^6}{240^6}\right) (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$\text{new } E_p = -376.106\,126\,2 \text{ J mol}^{-1}$$

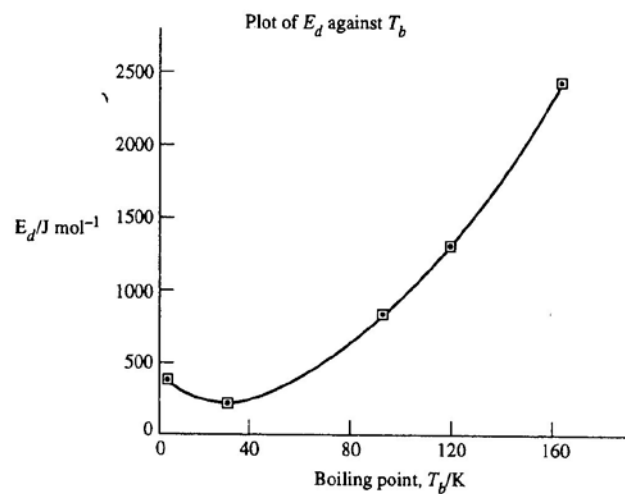
The values of  $-E_d/\text{J mol}^{-1}$  are then:

	He	Ne	Ar	Kr	Xe
For 500 pm	4.6	15.6	173	346	850
For $r$	376	228	895	1321	2420

If each Ar atom has 12 nearest neighbors, the estimated enthalpy of vaporization is

$$\left(\frac{12}{2}\right) \times (895 \text{ J mol}^{-1}) = 5370 \text{ J mol}^{-1}$$

This is not bad agreement considering the simplicity of the model.



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**\*17.18.** Estimate the interaction energy between an argon atom and a water molecule at a separation of 600 pm, which is approximately the distance of closest approach. The necessary data are: H<sub>2</sub>O: dipole moment,  $\mu = 6.18 \times 10^{-30}$  C m; Ar: polarizability,  $\alpha = 1.63 \times 10^{-30}$  m<sup>3</sup>.

Argon forms a solid hydrate, Ar·5H<sub>2</sub>O, but the binding energy between Ar and H<sub>2</sub>O is about 40 kJ mol<sup>-1</sup>, which is a good deal larger than the energy calculated from the dipole moment and polarizability. Suggest a reason for this discrepancy.

**Solution:**

Given:  $r = 600$  pm,  $\mu_{\text{H}_2\text{O}} = 6.18 \times 10^{-30}$  C m,  $\alpha_{\text{Ar}} = 1.63 \times 10^{-30}$  m<sup>3</sup>,  $E_{\text{binding}} = 40$  kJ mol<sup>-1</sup>

Required:  $E_{\text{interaction}}$ , explain the discrepancy

The interaction energy, with  $\epsilon = 1$ , is given by Eq. 17.18

$$E_p = -\frac{\alpha\mu^2}{2\pi\epsilon_0 r^6}$$

Since only H<sub>2</sub>O has a permanent dipole, the potential energy is halved, giving,

$$E_p = -\frac{\alpha\mu^2}{4\pi\epsilon_0 r^6}$$

Solving for interaction energy of Ar·H<sub>2</sub>O gives,

$$E_p = -\frac{(1.63 \times 10^{-30} \text{ m}^3)(6.18 \times 10^{-30} \text{ C m})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(6.00 \times 10^{-10} \text{ m})^6}$$

$$E_p = -1.199\,244\,32 \times 10^{-23} \text{ J}$$

$$\boxed{E_p = -1.20 \times 10^{-23} \text{ J}}$$

$$E_p = (-1.199\,244\,32 \times 10^{-23} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_p = 7.221\,849\,302 \text{ J mol}^{-1}$$

$$\boxed{E_p = 7.22 \times 10^{-3} \text{ kJ mol}^{-1}}$$

This value is far lower than the binding energy between  $\text{Ar} \cdot 5\text{H}_2\text{O}$  of  $40 \text{ kJ mol}^{-1}$  since there would be additional hydrogen bonding between neighbouring water molecules.

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**\*17.19. a.** The Lennard-Jones potential

$$E = -\frac{A}{r^6} + \frac{B}{r^n}$$

can be formulated in a different way by expressing  $A$  and  $B$  in terms of the minimum energy  $E_{\min}$  and the value  $r_0$  of  $r$  at the minimum energy. Obtain the expression for  $E$  in terms of  $E_{\min}$  and  $r_0$ .

**b.** If  $r^*$  is the value of  $r$  when  $E = 0$ , obtain the relationship between  $r^*$  and  $r_0$ .

**c.** The Lennard-Jones potential is often used with  $n = 12$ , and the equations are then simpler. Obtain  $E$  in terms of  $E_{\min}$  and  $r_0$  and in terms of  $E_{\min}$  and  $r^*$ , for this special case of  $n = 12$ .

**Solution:**

Given: Lennard-Jones potential

Required: **a.**  $E$  in terms of  $E_{\min}$  and  $r_0$

**b.** relationship between  $r^*$  and  $r_0$

**c.**  $E$  in terms of  $E_{\min}$  and  $r_0$ , and in terms of  $E_{\min}$  and  $r^*$  for  $n = 12$

**a.** We begin by taking the derivative of the Lennard-Jones potential and set it equal to zero. The resulting value of  $r$  corresponds to  $r_0$ .

$$E = -\frac{A}{r^6} + \frac{B}{r^n}$$

$$\frac{dE}{dr} = \frac{6A}{r_0^7} - \frac{nB}{r_0^{n+1}} = 0$$

$$\frac{6A}{r_0^7} = \frac{nB}{r_0^{n+1}}$$

Rearranging to obtain expressions for  $A$  and  $B$  we get,

$$A = \frac{nBr_0^{6-n}}{6} \quad \text{and} \quad B = \frac{6Ar_0^{n-6}}{n}$$

After substitution, the minimum energy becomes,

$$E_{\min} = -\frac{A}{r_0^6} + \frac{1}{r_0^n} \left( \frac{6Ar_0^{n-6}}{n} \right)$$

$$E_{\min} = -\frac{A}{r_0^6} + \frac{6A}{nr_0^6}$$

Therefore  $A$  can be written as,

$$A = \frac{nr_0^6 E_{\min}}{6-n}$$

Similarly, we determine  $B$  as,

$$B = \frac{6r_0^n E_{\min}}{6-n}$$

Then, substituting back into the original equation, we have  $E$  in terms of  $E_{\min}$  and  $r_0$ .

$$E = -\frac{1}{r^6} \left( \frac{nr_0^6 E_{\min}}{6-n} \right) + \frac{1}{r^n} \left( \frac{6r_0^n E_{\min}}{6-n} \right)$$

$$E = -\left( \frac{n}{6-n} \right) \frac{r_0^6}{r^6} E_{\min} + \left( \frac{6}{6-n} \right) \frac{r_0^n}{r^n} E_{\min}$$

$$\boxed{\frac{E}{E_{\min}} = -\frac{n}{6-n} \left( \frac{r_0}{r} \right)^6 + \frac{6}{6-n} \left( \frac{r_0}{r} \right)^n}$$

b. If  $r^*$  is the value of  $r$  when  $E = 0$ , then from the Lennard-Jones potential we have,

$$0 = -\frac{A}{(r^*)^6} + \frac{B}{(r^*)^n}$$

Rearranging this expression for  $r^*$  we get,

$$\frac{A}{(r^*)^6} = \frac{B}{(r^*)^n}$$

$$\frac{(r^*)^n}{(r^*)^6} = \frac{B}{A}$$

$$(r^*)^{n-6} = \frac{B}{A}$$

Using the expressions for  $A$  and  $B$  derived above we obtain the relationship between  $r^*$  and  $r_0$

$$(r^*)^{n-6} = \left( \frac{6r_0^n E_{\min}}{6-n} \right) \div \left( \frac{nr_0^6 E_{\min}}{6-n} \right)$$

$$(r^*)^{n-6} = \left( \frac{6r_0^n \cancel{E_{\min}}}{\cancel{6-n}} \right) \left( \frac{\cancel{6-n}}{nr_0^6 \cancel{E_{\min}}} \right)$$

$$(r^*)^{n-6} = \frac{6r_0^n}{nr_0^6}$$

$$(r^*)^{n-6} = \frac{6}{n} (r_0)^{n-6}$$

$$\boxed{\left( \frac{r^*}{r_0} \right)^{n-6} = \frac{6}{n}}$$

c. For  $n = 12$  we use the result from part a. to get  $E$  in terms of  $E_{\min}$  and  $r_0$ , and in terms of  $E_{\min}$  and  $r^*$ .

$$\frac{E}{E_{\min}} = -\frac{12}{6-12} \left( \frac{r_0}{r} \right)^6 + \frac{6}{6-12} \left( \frac{r_0}{r} \right)^{12}$$

$$\boxed{E = E_{\min} \left( 2 \left( \frac{r_0}{r} \right)^6 - \left( \frac{r_0}{r} \right)^{12} \right)}$$

For  $n = 12$ , we get  $r_0$  from the result of part b.

$$\left( \left( \frac{r^*}{r_0} \right)^{-1} \right)^{n-6} = \left( \frac{6}{n} \right)^{-1}$$

$$\left( \frac{r_0}{r^*} \right)^{n-6} = \frac{n}{6}$$

$$\left( \frac{r_0}{r^*} \right)^{12-6} = \frac{12}{6}$$

$$\left( \frac{r_0}{r^*} \right)^6 = 2$$

$$r_0^6 = 2(r^*)^6$$

Therefore,

$$E = E_{\min} \left( 2 \times 2 \left( \frac{r^*}{r} \right)^6 - \left( \frac{(2(r^*)^6)^2}{r} \right)^{12} \right)$$

$$E = E_{\min} \left( 4 \left( \frac{r^*}{r} \right)^6 - 4 \left( \frac{r^*}{r} \right)^{12} \right)$$

$$\boxed{E = 4E_{\min} \left( \left( \frac{r^*}{r} \right)^6 - \left( \frac{r^*}{r} \right)^{12} \right)}$$

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CHAPTER

# 18

Surface Chemistry  
and Colloids

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Physical Chemistry

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Problems and Solutions

## Chapter 18

## Adsorption Isotherms

**18.1.** A surface is half-covered by a gas when the pressure is 1 bar. If the simple Langmuir isotherm (Eq. 18.6) applies:

- What is  $K/\text{bar}^{-1}$ ?
- What pressures give 75%, 90%, 99%, 99.9% coverage?
- What coverage is given by pressures of 0.1 bar, 0.5 bar, 1000 bar?

[Solution](#)

**18.2.** Show that, if  $V$  is the volume of gas adsorbed at pressure  $P$ , and the Langmuir isotherm is obeyed, a plot of  $P/V$  against  $P$  is linear. Explain how, from such a plot, the volume  $V_0$  corresponding to complete coverage and the isotherm constant  $K$  can be determined.

[Solution](#)

**18.3.** The following results were reported by Langmuir for the adsorption of nitrogen on mica at 20 °C:

Pressure/atm	2.8	4	6	9.4	17.1	33.5
Amount of gas adsorbed/ $\text{mm}^3$ at 20 °C and 1 atm	12	15.1	19	23.9	28.2	33

- Make a linear plot of these values in order to test the Langmuir isotherm, Eq. 18.6. If it applies, evaluate the constant  $K$ .
- Suppose that  $10^{15}$  molecules cover  $1 \text{ cm}^2$  of the surface. Make an estimate of the effective surface area in Langmuir's experiment.

[Solution](#)

**18.4.** **a.** Show that for small coverages a system obeying the Langmuir isotherm will give a linear plot of  $\ln(\theta/P)$  against  $P$ , with a slope of unity.  
**b.** What is the slope if  $\ln(V_a/P)$  is plotted against  $V_a$  at small coverages? ( $V_a$  is the volume of gas adsorbed.)

[Solution](#)

**18.5.** The following are the volumes of ammonia, reduced to STP, adsorbed by 1 g of charcoal at 0 °C:

Pressure/kPa	6.8	13.5	26.7	53.1	79.4
Volume/cm <sup>3</sup>	74	111	147	177	189

Make a plot to see if the data are consistent with the Langmuir isotherm. If so, evaluate the constants  $K$  and  $V_0$ , the volume adsorbed when the surface is saturated.

[Solution](#)

**18.6. a.** Suggest a method of making a linear plot to test the applicability of the Brunauer, Emmett, and Teller (BET) isotherm (Eq. 18.25) when volumes adsorbed,  $V$ , are known at various pressures.

**b.** Show that the BET equation reduces to the Langmuir isotherm when  $P_0 \gg P$ .

[Solution](#)

**18.7.** The following data were obtained for the adsorption of krypton on a 1.21 g sample of a porous solid:

Pressure/Torr	1.11	3.08
Volume adsorbed/cm <sup>3</sup> (STP)	1.48	1.88

If the saturation vapor pressure is 19.0 Torr, estimate a surface area for the solid, assuming that a molecule of krypton occupies an area of  $2.1 \times 10^{-21} \text{ m}^2$ .

[Solution](#)

**\*18.8.** Derive the equation

$$\frac{\theta}{1-\theta} = c_g^{1/2} \frac{h^{3/2}}{(2\pi m k_B T)^{3/4}} \frac{b_a}{b_g^{1/2}} \exp\left(\frac{-\Delta E_0}{2RT}\right)$$

For the case of adsorption with dissociation (i.e.,  $A_2 + 2S \rightleftharpoons 2(S-A)$ );  $\Delta E_0$  is the energy of adsorption per mole.

[Solution](#)

**\*18.9.** Derive the equation

$$c_a = c_g \frac{h}{(2\pi m k_B T)^{1/2}} \frac{b_a}{b_g} \exp\left(\frac{-\Delta E_0}{2RT}\right)$$

For the case of adsorption where the adsorbed molecules are completely mobile on the surface (i.e., have two degrees of translational freedom).

[Solution](#)

### Kinetics of Surface Reactions

**18.10.** A first-order surface reaction is proceeding at a rate of  $1.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$  and has a rate constant  $2.0 \times 10^{-3} \text{ s}^{-1}$ . What will be the rate and the rate constant if

- the surface area is increased by a factor of 10?
  - the amount of gas is increased tenfold at constant pressure and temperature?
- If these values of  $v$  and  $k$  apply to a reaction occurring on the surface of a spherical vessel of radius 10 cm:
- What will be the rate and rate constant in a spherical vessel, of the same material, of radius 100 cm, at the same pressure and temperature?
  - Define a new rate constant  $k'$  that is independent of the gas volume  $V$  and the area  $S$  of the catalyst surface.
  - What would be its SI unit?

[Solution](#)

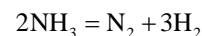
**18.11.** A zero-order reaction is proceeding at a rate of  $2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$  and a rate constant  $2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ .

- How will the changes a, b, and c in Problem 18.10 affect the rate and the rate constant in this case?
- Again, define a rate constant that is independent of  $S$  and  $V$ .
- What would be its SI unit?

[Solution](#)



**18.12.** The decomposition of ammonia on platinum,



is first order in  $\text{NH}_3$  and the rate is inversely proportional to the hydrogen concentration (Eq. 18.39). Write the differential rate equation for the rate of formation of hydrogen,  $dx/dt$ , in terms of the initial concentration of ammonia,  $a_0$ , and the concentration  $x$  of hydrogen at time  $t$ .

[Solution](#)

**\*18.13.** On the basis of the mechanism given on p. 943, derive an expression for the rate of formation of hydrogen atoms when hydrogen gas is in contact with hot tungsten. Under what conditions is the order of reaction one-half?

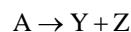
[Solution](#)

**18.14.** A unimolecular surface reaction is inhibited by a poison I and obeys Eq. 18.36. If  $E$  is the activation energy corresponding to the reaction of the adsorbed substrate molecule (i.e., corresponding to  $k$ ) and  $\Delta H_A$  and  $\Delta H_I$  are the enthalpies of adsorption of A and I, what is the activation energy

- a. at very low concentration of A and I?
- b. at a very high concentration of A and a very low concentration of I?
- c. at a very low concentration of A and a very high concentration of I?

[Solution](#)

**18.15.** Suppose that a reaction



Occurs initially as a homogeneous first-order reaction (rate constant  $k$ ) but that the product Z is adsorbed on the surface and catalyzes the reaction according to a law that is zero order in A and first order in Z (i.e., the term in the rate equation is  $k_c [\text{Z}]$ ). Obtain a differential equation for the rate of appearance of Z, and integrate it to give  $z$  as a function of time.

[Solution](#)

**18.16.** Suggest explanations for the following observations, in each case writing an appropriate rate equation based on a Langmuir isotherm:

- a. The decomposition of phosphine ( $\text{PH}_3$ ) on tungsten is first order at low pressures and zero order at higher pressures, the activation energy being higher at the higher pressures.
- b. The decomposition of ammonia on molybdenum is retarded by the product nitrogen, but the rate does not approach zero as the nitrogen pressure is increased.
- c. On certain surfaces (e.g., Au) the hydrogen-oxygen reaction is first order in hydrogen and zero order in oxygen, with no decrease in rate as the oxygen pressure is greatly increased.
- d. The conversion of para-hydrogen into ortho-hydrogen is zero order on several transition metals.

[Solution](#)

### Surface Tension and Capillarity

**18.17.** The surface tension of water at  $20^\circ\text{C}$  is  $7.27 \times 10^{-2} \text{ N m}^{-1}$  and its density is  $0.998 \text{ g cm}^{-3}$ . Assuming a contact angle  $\theta$  of zero, calculate the rise of water at  $20^\circ\text{C}$  in a capillary tube of radius (a) 1 mm and (b)  $10^{-3} \text{ cm}$ . Take  $g = 9.81 \text{ m s}^{-2}$ . (Capillaries in a tree have radii of about  $10^{-3} \text{ cm}$ , but sap can rise in a tree to much greater heights than obtained in this calculation. The reason is that the rise of sap depends to a considerable extent on osmotic flow; because of evaporation the leaves contain solutes of higher concentration than the trunk of the tree, and osmotic flow therefore occurs to the leaves.)

[Solution](#)

**18.18.** The density of liquid mercury at  $273 \text{ K}$  is  $13.6 \text{ g cm}^{-3}$  and the surface tension is  $0.47 \text{ N m}^{-1}$ . If the contact angle is  $140^\circ$ , calculate the capillary depression in a tube of 1-mm diameter.

[Solution](#)

**18.19.** The density of water at  $20^\circ\text{C}$  is  $0.998 \text{ g cm}^{-3}$  and the surface tension is  $7.27 \times 10^{-2} \text{ N m}^{-1}$ . Calculate the ratio between the vapor pressure of a mist droplet having a mass of  $10^{-12} \text{ g}$  and the vapor pressure of water at a plane surface.

[Solution](#)

**18.20.** The two arms of a U-tube have radii of 0.05 cm and 0.10 cm. A liquid of density  $0.80 \text{ g cm}^{-3}$  is placed in the tube, and the height in the narrower arm is found to be 2.20 cm higher than that in the wider arm. Calculate the surface tension of the liquid, assuming  $\theta = 0$ .

[Solution](#)

**18.21.** A tube is placed in a certain liquid and the capillary rise is 1.5 cm. What would be the rise if the same tube were placed in another liquid that has half the surface tension and half the density of the first liquid? Assume that  $\theta = 0$  in both cases.

[Solution](#)

**18.22.** When a certain capillary tube is placed in water, the capillary rise is 2.0 cm. Suppose that the tube is placed in the water in such a way that only 1.0 cm is above the surface; will the water flow over the edge? Explain your answer.

[Solution](#)

**\*18.23.** A layer of benzene, of density  $0.8 \text{ g cm}^{-3}$ , is floating on water of density  $1.0 \text{ g cm}^{-3}$ , and a vertical tube of internal diameter 0.1 mm is inserted at the interface. It is observed that there is a capillary rise of 4.0 cm and that the contact angle is  $40^\circ$ . Calculate the interfacial tension between water and benzene.

[Solution](#)

**18.24.** A liter of water at  $20^\circ\text{C}$  is broken up into a spray in which the droplets have an average radius of  $10^{-5} \text{ cm}$ . If the surface tension of water at  $20^\circ\text{C}$  is  $7.27 \times 10^{-2} \text{ N m}^{-1}$ , calculate the Gibbs energy change when the droplets are formed.

[Solution](#)

### Surface Films

**18.25.** Benjamin Franklin demonstrated on a number of occasions that a teaspoonful of oil put on water would produce a layer half an acre in area (1 acre = 4840 square yards; 1 yard = 0.915 m). Assume a teaspoonful to be  $1 \text{ cm}^3$ , and estimate the thickness of the film.

[Solution](#)

**18.26.** A fatty acid was spread on the surface of water in a Langmuir film balance at 15 °C, and the following results obtained:

Area/cm <sup>2</sup> μg <sup>-1</sup>	5.7	28.2	507	1070	2200	11100
Surface pressure/ 10 <sup>-3</sup> N m <sup>-1</sup>	30	0.3	0.2	0.1	0.05	0.01

Estimate the molecular weight of the acid and the area per molecule when the film was fully compressed.

[Solution](#)

**18.27.** N. K. Adam carried out surface film studies using a Langmuir film balance 14.0 cm in width having a floating barrier 13.8 cm long. In one investigation he introduced 52.0 μg of 1-hexadecanol (C<sub>16</sub>H<sub>33</sub>OH) onto the surface and measured the force on the float at various lengths of the film, obtaining the following results:

Length/cm	Force on float/10 <sup>-5</sup> N
20.9	4.14
20.3	8.56
20.1	26.2
19.6	69.0
19.1	108.0
18.6	234
18.3	323
18.1	394
17.8	531

Estimate the area per molecule when the film was fully compressed.

[Solution](#)

**Essay Questions**

**18.28.** Describe some of the most important characteristics of a chemisorbed layer. In what ways does a physisorbed (van der Waals) layer differ?

**18.29.** Derive the Langmuir adsorption isotherms for two substances competitively adsorbed on a surface. Show how these equations interpret the kinetics of bimolecular surface reactions, distinguishing between Langmuir-Hinshelwood and Langmuir-Rideal mechanisms.

**18.30.** Explain clearly the distinction between inherent and induced heterogeneity of surfaces.

**18.31.** Explain the difference between lyophilic and lyophobic sols, with reference to some of the properties in which they differ.

**18.32.** What information can be obtained from light-scattering experiments on colloidal particles in aqueous solution?

**Solutions**

**18.1.** A surface is half-covered by a gas when the pressure is 1 bar. If the simple Langmuir isotherm (Eq. 18.6) applies:

- a. What is  $K/\text{bar}^{-1}$ ?
- b. What pressures give 75%, 90%, 99%, 99.9% coverage?
- c. What coverage is given by pressures of 0.1 bar, 0.5 bar, 1000 bar?

**Solution:**

Given: simple Langmuir isotherm applies,  $P = 1$  bar

Required: see above

- a. For a surface that is half-covered,  $\theta = 0.5$ . Using Eq. 18.6 for the simple Langmuir isotherm, we replace the concentration  $[A]$  by the pressure, to obtain the value of  $K$  in bar.

$$\theta = \frac{K[A]}{1 + K[A]}$$

$$0.5 = \frac{K \times 1 \text{ bar}}{1 + K \times 1 \text{ bar}}$$

$$0.5 + 0.5K = K$$

$$\boxed{K = 1 \text{ bar}}$$

- b. Here, we use a modified version of Eq. 18.6, with  $K$  replaced by  $P$ , in order to solve for the unknown pressure. We can derive a standard equation to solve for this particular problem as the initial pressure is 1 bar.

$$\theta = \frac{P \times 1 \text{ bar}}{1 + P \times 1 \text{ bar}}$$

$$\theta + P\theta = P$$

$$\theta = P - P\theta$$

$$\theta = P(1 - \theta)$$

$$P = \frac{\theta}{1 - \theta}$$

For 75% coverage:

$$P = \frac{0.75}{1 - 0.75} = \frac{0.75}{0.25}$$

$$\boxed{P = 3 \text{ bar}}$$

For 90% coverage:

$$P = \frac{0.90}{1 - 0.90} = \frac{0.90}{0.10}$$

$$\boxed{P = 9 \text{ bar}}$$

For 99% coverage:

$$P = \frac{0.99}{1 - 0.99} = \frac{0.99}{0.01}$$

$$\boxed{P = 99 \text{ bar}}$$

For 99.9% coverage:

$$P = \frac{0.999}{1 - 0.999} = \frac{0.999}{0.001}$$

$$\boxed{P = 999 \text{ bar}}$$

- c. This problem is similar to **b.**, but with pressure as the known variable and percent coverage as the unknown variable. We can slightly modify the previous derived equation as follow:

$$\theta = \frac{P \times 1 \text{ bar}}{1 + P \times 1 \text{ bar}}$$

$$\theta + P\theta = P$$

$$\theta(1 + P) = P$$

$$\theta = \frac{P}{1 + P}$$

For 0.1 bar pressure:

$$\theta = \frac{0.1}{1 + 0.1} = \frac{0.1}{1.1}$$

$$\theta = 0.09090909$$

$$\boxed{\theta = 0.091 \text{ or } 9.1\%}$$

For 0.5 bar pressure:

$$\theta = \frac{0.5}{1 + 0.5} = \frac{0.5}{1.5}$$

$$\theta = 0.33333333$$

$$\boxed{\theta = 0.33 \text{ or } 33\%}$$

For 1000 bar pressure:

$$\theta = \frac{1000}{1 + 1000} = \frac{1000}{1001}$$

$$\theta = 0.999000999$$

$$\boxed{\theta = 0.999 \text{ or } 99.9\%}$$

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**18.2.** Show that, if  $V$  is the volume of gas adsorbed at pressure  $P$ , and the Langmuir isotherm is obeyed, a plot of  $P/V$  against  $P$  is linear. Explain how, from such a plot, the volume  $V_0$  corresponding to complete coverage and the isotherm constant  $K$  can be determined.

**Solution:**

Given: Langmuir isotherm

Required: show that plot of  $P/V$  against  $P$  is linear, explanation

The Langmuir isotherm in terms of pressure  $P$  is, from Eq. 18.6,

$$\theta = \frac{KP}{1 + KP}$$
$$\theta = \frac{V}{V_0}$$

and therefore

$$\frac{V}{V_0} = \frac{KP}{1 + KP}$$

which rearranges to

$$\frac{P}{V} = \frac{1 + KP}{V_0 K} = \frac{1}{V_0 K} + \frac{P}{V_0}$$

A plot of  $P/V$  against  $P$  is therefore linear; the slope is  $1/V_0$  and the intercept on the  $P/V_0$  axis is  $1/V_0 K$ . The quantities  $V_0$  and  $K$  can thus be obtained separately.

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**18.3.** The following results were reported by Langmuir for the adsorption of nitrogen on mica at 20 °C:

Pressure/atm	2.8	4	6	9.4	17.1	33.5
Amount of gas adsorbed/mm <sup>3</sup> at 20 °C and 1 atm	12	15.1	19	23.9	28.2	33

- Make a linear plot of these values in order to test the Langmuir isotherm, Eq. 18.6. If it applies, evaluate the constant  $K$ .
- Suppose that  $10^{15}$  molecules cover 1 cm<sup>2</sup> of the surface. Make an estimate of the effective surface area in Langmuir's experiment.

**Solution:**

Given: above table

Required: test for Langmuir isotherm, constant  $K$ , effective surface area

We know that the amount of gas adsorbed  $x$  is proportional to the percent coverage  $\theta$ . Therefore,

$$x = \frac{aK[A]}{1 + K[A]}$$

However, instead of the concentration, pressure is given. To convert pressure in atmospheres to concentrations, we use the ideal gas law:

$$\frac{n}{V} = \frac{P}{RT} = \frac{(P \text{ atm})}{(0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})}$$

To convert the amount of gas adsorbed to moles:

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm})(V \text{ dm}^3)}{(0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})}$$

$$n = \frac{(V \text{ mm}^3)}{(0.08205 \text{ dm}^3 \text{ mol}^{-1})(293.15)} \times \frac{\text{dm}^3}{1000 \text{ mm}^3}$$

$$n = \frac{V/\text{mm}^3}{24\,052.9575 \text{ mol}^{-1}}$$

Thus, the table given above becomes

Concentration/mol dm <sup>-3</sup>	0.116	0.166	0.249	0.391	0.711	1.39
------------------------------------	-------	-------	-------	-------	-------	------

Amount of gas adsorbed/10 <sup>-7</sup> mol	4.99	6.28	7.90	9.94	11.7	13.7
---	------	------	------	------	------	------

a. A linear plot may be obtained by plotting 1/x against 1/[A]:

$$\frac{1}{x} = \frac{1}{aK[A]} + \frac{1}{a}$$

[A] <sup>-1</sup> /dm <sup>3</sup> mol <sup>-1</sup>	8.62	6.02	4.02	2.56	1.41	0.719
--	------	------	------	------	------	-------

x <sup>-1</sup> /10 <sup>6</sup> mol <sup>-1</sup>	2.00	1.59	1.27	1.01	0.85	0.73
--	------	------	------	------	------	------

From a plot of x<sup>-1</sup> against [A]<sup>-1</sup> or from linear regression,

$$a = 1.63 \times 10^{-6} \text{ mol}$$

$$K = 3.82 \text{ dm}^3 \text{ mol}^{-1}$$

Here the solution manual doesn't have a plot or linear regression. Maybe add the plot and the linear regression for clearer explanation?

b. Complete coverage corresponds to

$$(1.63 \times 10^{-6} \text{ mol}) \times (6.022 \times 10^{23} \text{ molecules mol}^{-1}) = 9.81586 \times 10^{17} \text{ molecules}$$

For  $10^{15}$  molecules that covers  $1 \text{ cm}^2$  of the surface, the effective surface area in Langmuir's experiment will be:

$$(9.81586 \times 10^{17} \text{ molecules}) \times \left( \frac{1 \text{ cm}^2}{10^{15} \text{ molecules}} \right) = 981.586 \text{ cm}^2$$

$$\boxed{\text{effective surface area: } 9.8 \times 10^2 \text{ cm}^2 \text{ or } 0.098 \text{ m}^2}$$

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- 18.4.** a. Show that for small coverages a system obeying the Langmuir isotherm will give a linear plot of  $\ln (\theta/P)$  against  $P$ , with a slope of unity.  
 b. What is the slope if  $\ln (V_a/P)$  is plotted against  $V_a$  at small coverages? ( $V_a$  is the volume of gas adsorbed.)

**Solution:**

Given: small coverages, see above

Required: see above

- a. In order to derive the equation for the plot of  $\ln (\theta/P)$  against  $P$ , we first start with Eq.18.7,

$$1 - \theta = \frac{1}{1 + KP} \quad (1)$$

Rearranging,

$$\begin{aligned} (1 - \theta)(1 + KP) &= 1 \\ 1 + KP - \theta - \theta KP &= 1 \\ \theta &= KP - \theta KP \\ \theta &= KP(1 - \theta) \end{aligned} \quad (2)$$

Taking the natural logarithm on both sides yield:

$$\begin{aligned} \frac{\theta}{P} &= K(1 - \theta) \\ \ln \frac{\theta}{P} &= \ln K + \ln(1 - \theta) \end{aligned} \quad (3)$$

$$\ln \frac{\theta}{P} \approx \ln K - \theta \quad \text{if } \theta \ll 1 \quad (4)$$

A plot of  $\ln (\theta/P)$  against  $\theta$  is thus linear with a slope of -1.

The problem as to prove that plot of  $\ln (\theta/P)$  against  $P$  is linear, instead of  $\ln (\theta/P)$  against  $\theta$ . The solution manual is also wrong.

b. Since  $\theta = V/V_0$ , Eq. (4) can be written as

$$\ln\left(\frac{V}{P}\right) - \ln V_0 \approx \ln K - \frac{V}{V_0}$$

A plot of  $\ln(V/P)$  against  $V$  thus has a slope of  $-1/V_0$ .

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**18.5.** The following are the volumes of ammonia, reduced to STP, adsorbed by 1 g of charcoal at 0 °C:

Pressure/kPa	6.8	13.5	26.7	53.1	79.4
Volume/cm <sup>3</sup>	74	111	147	177	189

Make a plot to see if the data are consistent with the Langmuir isotherm. If so, evaluate the constants  $K$  and  $V_0$ , the volume adsorbed when the surface is saturated.

**Solution:**

Given: above table

Required: constant  $K$  and  $V_0$

The Langmuir isotherm can be used in the form

$$\frac{V}{V_0} = \frac{KP}{1 + KP} \quad \text{or} \quad \frac{1}{V} = \frac{1}{V_0 KP} + \frac{1}{V_0}$$

The data are plotted as  $1/V$  against  $1/P$  in the accompanying figure. The Langmuir isotherm is obeyed, with

$$V_0 = 222 \text{ cm}^3 \quad \text{and} \quad K = 7.35 \times 10^{-2} \text{ kPa}^{-1}$$

[image]

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- 18.6.** a. Suggest a method of making a linear plot to test the applicability of the Brunauer, Emmett, and Teller (BET) isotherm (Eq. 18.25) when volumes adsorbed,  $V$ , are known at various pressures.  
b. Show that the BET equation reduces to the Langmuir isotherm when  $P_0 \gg P$ .

**Solution**

Given: volumes at various pressures

Required: see above

- a. The BET isotherm can be tested in a number of ways, for example by plotting  $P/V(P_0 - P)$  against  $P$ .  
b. If  $P_0 \gg P$ , the isotherm becomes

$$\frac{P}{V} = \frac{1}{V_0 K} + \frac{P}{V_0}$$

The fraction covered  $\theta = \frac{V}{V_0}$  and therefore,

$$\frac{P}{\theta} = \frac{1}{K} + P$$

or

$$\theta = \frac{KP}{1 + KP}$$

Which is the Langmuir isotherm.

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**18.7.** The following data were obtained for the adsorption of krypton on a 1.21 g sample of a porous solid:

Pressure/Torr	1.11	3.08
Volume adsorbed/cm <sup>3</sup> (STP)	1.48	1.88

If the saturation vapor pressure is 19.0 Torr, estimate a surface area for the solid, assuming that a molecule of krypton occupies an area of  $2.1 \times 10^{-21} \text{ m}^2$ .

**Solution:**

Given: above table, vapor pressure = 19.0 Torr, area/molecule of krypton =  $2.1 \times 10^{-21} \text{ m}^2$ .

Required: surface area for the solid

Inserting of the data into the BET isotherm (Eq. 18.25) gives two simultaneous equations:

$$\frac{PP_0}{V(P_0 - P)} = \frac{1}{V_0 K} + \frac{P}{V_0}$$

first set:

$$\frac{1.11 \times 19.0}{1.48(19.0 - 1.11)} = \frac{1}{V_0 K} + \frac{1.11}{V_0}$$

$$0.796 \ 534 \ 376 = \frac{1}{V_0 K} + \frac{1.11}{V_0} \quad (1)$$

second set:

$$\frac{3.08 \times 19.0}{1.88(19.0 - 3.08)} = \frac{1}{V_0 K} + \frac{3.08}{V_0}$$

$$1.955 \ 254 \ 998 = \frac{1}{V_0 K} + \frac{3.08}{V_0} \quad (2)$$

Now we have two equations and two unknowns and we can therefore solve for the values of  $K$  and  $V_0$

using equation (1) to isolate an expression for  $K$

$$0.796\,534\,376 = \frac{1}{V_0 K} + \frac{1.11}{V_0}$$

$$0.796\,534\,376 V_0 K = 1 + 1.11 K$$

$$0.796\,534\,376 V_0 K - 1.11 K = 1$$

$$K (0.796\,534\,376 V_0 - 1.11) = 1$$

$$K = \frac{1}{0.796\ 534\ 376V_0 - 1.11}$$

replace the above expression into equation (2)

$$1.955\ 254\ 998 = \frac{1}{V_0 K} + \frac{3.08}{V_0}$$

$$1.955\ 254\ 998 = \frac{1}{V_0 \left( \frac{1}{0.796\ 534\ 376V_0 - 1.11} \right)} + \frac{3.08}{V_0}$$

$$1.955\ 254\ 998 = \frac{0.796\ 534\ 376V_0 - 1.11 + 3.08}{V_0}$$

$$1.955\ 254\ 998V_0 = 0.796\ 534\ 376V_0 + 1.97$$

$$1.158\ 720\ 56V_0 = 1.97$$

$$V_0 = \frac{1.97}{1.158\ 720\ 56}$$

$$V_0 = 1.700\ 151\ 069\ \text{cm}^3$$

substitute this value into equation (1) or (2) will solve for the value of  $K$

$$0.796\ 534\ 376 = \frac{1}{V_0 K} + \frac{1.11}{V_0}$$

$$0.796\ 534\ 376 = \frac{1}{1.700\ 151\ 069K} + \frac{1.11}{1.700\ 151\ 069}$$

$$0.796\ 534\ 376 = \frac{1}{1.700\ 151\ 069K} + 0.652\ 883\ 158$$

$$0.143\ 651\ 217 = \frac{1}{1.700\ 151\ 069K}$$

$$K = \frac{1}{(0.143\ 651\ 217)(1.700\ 151\ 069)}$$

$$K = 4.094\ 521\ 704\ \text{Torr}^{-1}$$

Now that we have the value of  $V_0$ , it is possible to determine the number of molecules

At S.T.P., 22.7 L = 22 700 cm<sup>3</sup> is the volume occupied by 1 mol. A volume of 1.700 151 069 cm<sup>3</sup> thus contains

$$\frac{1 \text{ mol}}{22\,700 \text{ cm}^3} \times 1.700\,151\,069 \text{ cm}^3 = 7.489\,652\,286 \times 10^{-5} \text{ mol}$$

$$(7.489\,652\,286 \times 10^{-5} \text{ mol}) \times (6.022 \times 10^{23} \text{ molecules mol}^{-1}) = 4.510\,268\,607 \times 10^{19} \text{ molecules}$$

The surface area is thus

$$\frac{2.1 \times 10^{-21} \text{ m}^2}{\text{molecule}} \times 4.510\,268\,607 \times 10^{19} \text{ molecules} = 0.094\,715\,64 \text{ m}^2$$

$$\boxed{\text{surface area} = 947 \text{ cm}^2}$$

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**\*18.8.** Derive the equation

$$\frac{\theta}{1-\theta} = c_g^{1/2} \frac{h^{3/2}}{(2\pi m k_B T)^{3/4}} \frac{b_a}{b_g^{1/2}} \exp\left(\frac{-\Delta E_0}{2RT}\right)$$

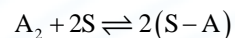
For the case of adsorption with dissociation (i.e.,  $A_2 + 2S \rightleftharpoons 2(S-A)$ );  $\Delta E_0$  is the energy of adsorption per mole.

**Solution:**

Given: see above

Required: derivation for the case of adsorption with dissociation

The process is



and

$$K_c = \frac{c_a^2}{c_g c_s^2} = \frac{N_a^2}{(N_g/V) N_s^2}$$

$$K_c = \left(\frac{\theta}{1-\theta}\right)^2 \frac{1}{c_g}$$

In terms of partition functions,

$$K_c = \frac{q_a^2}{q_g q_s^2} \exp\left(\frac{-\Delta E_0}{RT}\right)$$

$$K_c = \frac{h^3 b_a^2}{(2\pi m k_B T)^{3/2} b_g} \exp\left(\frac{-\Delta E_0}{RT}\right) \quad (\text{if } q_s = 1)$$

Therefore

$$\frac{\theta}{1-\theta} = c_g^{1/2} \frac{h^{3/2} b_a}{(2\pi m k_B T)^{3/4} b_g^{1/2}} \exp\left(\frac{-\Delta E_0}{2RT}\right)$$

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**\*18.9.** Derive the equation

$$c_a = c_g \frac{h}{(2\pi m k_B T)^{1/2}} \frac{b_a}{b_g} \exp\left(\frac{-\Delta E_0}{2RT}\right)$$

For the case of adsorption where the adsorbed molecules are completely mobile on the surface (i.e., have two degrees of translational freedom).

**Solution:**

Given: see above

Required: derivation for adsorption where the adsorbed molecules are mobile on the surface

The adsorption centers need no longer be regarded as reactants; the equilibrium is between gas molecules and molecules forming the two-dimensional layer:

$$K_c = \frac{c_a}{c_g} = \frac{N_a/S}{N_g/V}$$

$$K_c = \frac{\frac{(2\pi m k_B T)}{h^2} b_a \exp\left(\frac{-\Delta E_0}{RT}\right)}{\frac{(2\pi m k_B T)^{3/2}}{h^3} b_g}$$

Therefore

$$c_a = c_g \frac{h}{(2\pi m k_B T)^{1/2}} \frac{b_a}{b_g} \exp\left(\frac{-\Delta E_0}{RT}\right)$$

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**18.10.** A first-order surface reaction is proceeding at a rate of  $1.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$  and has a rate constant  $2.0 \times 10^{-3} \text{ s}^{-1}$ . What will be the rate and the rate constant if

- the surface area is increased by a factor of 10?
- the amount of gas is increased tenfold at constant pressure and temperature?  
If these values of  $v$  and  $k$  apply to a reaction occurring on the surface of a spherical vessel of radius 10 cm:
- What will be the rate and rate constant in a spherical vessel, of the same material, of radius 100 cm, at the same pressure and temperature?
- Define a new rate constant  $k'$  that is independent of the gas volume  $V$  and the area  $S$  of the catalyst surface.
- What would be its SI unit?

**Solution:**

Given: reaction rate =  $1.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ , rate constant =  $2.0 \times 10^{-3} \text{ s}^{-1}$

Required: see above

- a.** The rate and the rate constant are both increased by a factor of 10:

$$v = 1.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}; \quad k = 2.0 \times 10^{-2} \text{ s}^{-1}$$

- b.** The rate of conversion ( $\text{mol s}^{-1}$ ) remains the same, but since the volume is increased by a factor of 10, the rate is reduced by a factor of 10, as is the rate constant:

$$v = 1.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}; \quad k = 2.0 \times 10^{-4} \text{ s}^{-1}$$

- c.** Increasing the radius by a factor of 10 increases the surface area by a factor of 100 and the volume by a factor of 1000. The rate and the rate constant are thus reduced by a factor of 10:

$$v = 1.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}; \quad k = 2.0 \times 10^{-4} \text{ s}^{-1}$$

- d.** Since  $k$  is proportional to  $S$  and inversely proportional to  $V$ , the constant  $k' = \frac{kV}{S}$  is independent of  $V$  and  $S$ .

- e.** Its SI units is  $\text{m s}^{-1}$ .

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**18.11.** A zero-order reaction is proceeding at a rate of  $2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$  and a rate constant  $2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ .

- a. How will the changes a, b, and c in Problem 18.10 affect the rate and the rate constant in this case?
- b. Again, define a rate constant that is independent of  $S$  and  $V$ .
- c. What would be its SI unit?

**Solution:**

Given: reaction rate =  $2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ , rate constant =  $2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$

Required: see above

The arguments here are the same as in Problem 18.10, and thus,

a. (a')  $k = 2.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$

$$\nu = 2.5 \times 10^{-2} \text{ s}^{-1}$$

(b')  $k = 2.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

$$\nu = 2.5 \times 10^{-4} \text{ s}^{-1}$$

(c')  $k = 2.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

$$\nu = 2.5 \times 10^{-4} \text{ s}^{-1}$$

b.  $k' = kV/S$

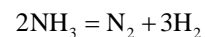
c.  $\text{mol m}^{-2} \text{ s}^{-1}$

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**18.12.** The decomposition of ammonia on platinum,



is first order in  $\text{NH}_3$  and the rate is inversely proportional to the hydrogen concentration (Eq. 18.39). Write the differential rate equation for the rate of formation of hydrogen,  $dx/dt$ , in terms of the initial concentration of ammonia,  $a_0$ , and the concentration  $x$  of hydrogen at time  $t$ .

**Solution:**

Given: see above

Required: see above

To solve this problem, we can use a table that shows the initial concentrations of the reactants and the products and the concentration after a time  $t$ , assuming that  $x$  amount of  $3\text{H}_2$  has been consumed.

	$2\text{NH}_3$	=	$\text{N}_2$	+	$3\text{H}_2$
Initial concentrations	$a_0$		0		0
Concentrations after time $t$ :	$a_0 - \frac{2x}{3}$		$\frac{x}{3}$		$x$

$$\frac{dx}{dt} = \frac{k \left( a_0 - \frac{2x}{3} \right)}{x}$$

$$\frac{dx}{dt} = \frac{3ka_0 - 2kx}{3x}$$

$$\frac{dx}{dt} = \frac{ka_0}{x} - \frac{2k}{3}$$

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**\*18.13.** On the basis of the mechanism given on p. 943, derive an expression for the rate of formation of hydrogen atoms when hydrogen gas is in contact with hot tungsten. Under what conditions is the order of reaction one-half?

**Solution:**

Given: see above

Required: derivation for the rate of formation of hydrogen atoms

From Eq. 18.14, the fraction of bare surface is

$$K^{1/2} [\text{H}_2]^{1/2} \gg 1 \quad 1 - \theta = \frac{1}{1 + K^{1/2} [\text{H}_2]^{1/2}}$$

Rate of H atom formation is thus,

$$\begin{aligned} \nu &= k(1 - \theta)[\text{H}_2] \\ \nu &= \frac{k[\text{H}_2]}{1 + K^{1/2} [\text{H}_2]^{1/2}} \end{aligned}$$

Kinetics are one-half order when  $K^{1/2} [\text{H}_2]^{1/2} \gg 1$ ; i.e., at high pressure when the surface is fully covered:

$$\nu = \frac{k}{K^{1/2}} [\text{H}_2]^{1/2}$$

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**18.14.** A unimolecular surface reaction is inhibited by a poison I and obeys Eq. 18.36. If  $E$  is the activation energy corresponding to the reaction of the adsorbed substrate molecule (i.e., corresponding to  $k$ ) and  $\Delta H_A$  and  $\Delta H_I$  are the enthalpies of adsorption of A and I, what is the activation energy

- a. at very low concentration of A and I?
- b. at a very high concentration of A and a very low concentration of I?
- c. at a very low concentration of A and a very high concentration of I?

**Solution:**

Given: see above

Required: see above

We know that  $k \propto \exp\left(\frac{-E}{RT}\right)$ ,  $K \propto \exp\left(\frac{-\Delta H_A}{RT}\right)$  and  $K_i \propto \exp\left(\frac{-\Delta H_I}{RT}\right)$

a.  $\nu = kK[A] \propto \exp\left[\frac{-(E + \Delta H_A)}{RT}\right]$

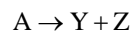
b.  $\nu = k \propto \exp\left(\frac{-E}{RT}\right)$

c.  $\nu = \frac{kK[A]}{K_i[I]} \propto \exp\left[\frac{-(E + \Delta H_A - \Delta H_I)}{RT}\right]$

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**18.15.** Suppose that a reaction



Occurs initially as a homogeneous first-order reaction (rate constant  $k$ ) but that the product  $Z$  is adsorbed on the surface and catalyzes the reaction according to a law that is zero order in  $A$  and first order in  $Z$  (i.e., the term in the rate equation is  $k_c [Z]$ ). Obtain a differential equation for the rate of appearance of  $Z$ , and integrate it to give  $Z$  as a function of time.

**Solution:**

Given: see above

Required: obtain differential equation, integration to give  $Z$  as a function of time

We can start by constructing a table similar to Problem 18.12

	A	→	Y	+	Z
Initially:	$a_0$		0		0
At time $t$ :	$a_0 - z$		$z$		$z$

$$\frac{dz}{dt} = k(a_0 - z) + k_s z$$

$$\frac{dz}{dt} = ka_0 - kz + k_s z$$

$$\frac{dz}{dt} = ka_0 + (k_s - k)z$$

$$\frac{dz}{ka_0 + (k_s - k)z} = dt$$

Let  $ka_0 + (k_s - k)z = y$ ;  $dy = (k_s - k)dz$  and  $dz = \frac{dy}{(k_s - k)}$

$$\frac{1}{(k_s - k)} \int \frac{dy}{y} = \int dt$$

$$\frac{1}{(k_s - k)} \ln(y) = t + I$$

substitute:

$$\frac{1}{(k_s - k)} \ln[ka_0 + (k_s - k)z] = t + I$$

In order to solve for the constant I, we apply the boundary condition,  $z = 0, t = 0$

$$\frac{1}{(k_s - k)} \ln[ka_0 + (k_s - k)0] = 0 + I$$

$$\frac{1}{(k_s - k)} \ln(ka_0) = I$$

Now, we substitute the expression for the constant I back in to the integrated equation to obtain an expression for  $z$ .

$$\frac{1}{(k_s - k)} \ln [ka_0 + (k_s - k)z] = t + I$$

$$\frac{1}{(k_s - k)} \ln [ka_0 + (k_s - k)z] = t + \frac{1}{(k_s - k)} \ln (ka_0)$$

$$\frac{1}{(k_s - k)} \{ \ln [ka_0 + (k_s - k)z] - \ln (ka_0) \} = t$$

$$\frac{1}{(k_s - k)} \ln \left[ \frac{ka_0 + (k_s - k)z}{ka_0} \right] = t$$

$$\ln \left[ \frac{ka_0 + (k_s - k)z}{ka_0} \right] = t(k_s - k)$$

$$\frac{ka_0 + (k_s - k)z}{ka_0} = \exp [t(k_s - k)]$$

$$ka_0 + (k_s - k)z = ka_0 \exp [t(k_s - k)]$$

$$(k_s - k)z = ka_0 \exp [t(k_s - k)] - ka_0$$

$$z = \frac{ka_0 \exp [t(k_s - k)] - ka_0}{(k_s - k)}$$

$$z = \frac{ka_0}{(k_s - k)} \{ \exp [t(k_s - k)] - 1 \}$$

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**18.16.** Suggest explanations for the following observations, in each case writing an appropriate rate equation based on a Langmuir isotherm:

- The decomposition of phosphine ( $\text{PH}_3$ ) on tungsten is first order at low pressures and zero order at higher pressures, the activation energy being higher at the higher pressures.
- The decomposition of ammonia on molybdenum is retarded by the product nitrogen, but the rate does not approach zero as the nitrogen pressure is increased.
- On certain surfaces (e.g., Au) the hydrogen-oxygen reaction is first order in hydrogen and zero order in oxygen, with no decrease in rate as the oxygen pressure is greatly increased.
- The conversion of para-hydrogen into ortho-hydrogen is zero order on several transition metals.

**Solution:**

Given: Langmuir isotherm, information above

Required: suggest explanations

- a.** The general rate equation is Eq. 18.34. At low pressures the surface is sparsely covered and

$$v = kK[A]; \quad E_{a_{\text{observed}}} = E_{a_0} + \Delta H_{ad}$$

At high pressure it is fully covered and

$$v = k; \quad E_{a_{\text{observed}}} = E_{a_0} \text{ \& } \Delta H_{ad} < 0$$

- b.** Reaction occurs on certain surface sites on which  $\text{N}_2$  is not adsorbed. The rate equation is Eq. 18.36.
- c.** This is a Langmuir-Rideal mechanism. The general equation is Eq. 18.44;  $K_{\text{H}_2} [\text{H}_2]$  is small and  $K_{\text{O}_2} [\text{O}_2]$  is large, so that

$$v = k[\text{H}_2]$$

- d.** The mechanism is

[image]

with the surface fully covered. The rate is

$$v = k[\text{H}_2](1-\theta)^2$$

where  $1 - \theta$  is given by Eq. 18.15; thus

$$v = \frac{k}{K}$$

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**18.17.** The surface tension of water at 20 °C is  $7.27 \times 10^{-2} \text{ N m}^{-1}$  and its density is  $0.998 \text{ g cm}^{-3}$ . Assuming a contact angle  $\theta$  of zero, calculate the rise of water at 20 °C in a capillary tube of radius (a) 1 mm and (b)  $10^{-3} \text{ cm}$ . Take  $g = 9.81 \text{ m s}^{-2}$ . (Capillaries in a tree have radii of about  $10^{-3} \text{ cm}$ , but sap can rise in a tree to much greater heights than obtained in this calculation. The reason is that the rise of sap depends to a considerable extent on osmotic flow; because of evaporation the leaves contain solutes of higher concentration than the trunk of the tree, and osmotic flow therefore occurs to the leaves.)

**Solution:**

Given:  $T = 20 \text{ }^{\circ}\text{C}$ ,  $\gamma = 7.27 \times 10^{-2} \text{ N m}^{-1}$ ,  $\rho = 0.998 \text{ g cm}^{-3}$ ,  $\theta = 0^{\circ}$ ,  $g = 9.81 \text{ m s}^{-2}$   
 $r_1 = 1 \text{ mm}$ ,  $r_2 = 10^{-3} \text{ cm}$

Required: rise of water

According to Eq. 18.54, the capillary rise is given by

$$h = \frac{2\gamma}{\rho g r}$$

We first convert everything to SI units.

$$\rho = 0.998 \cancel{\text{ g}} \cancel{\text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \cancel{\text{ g}}} \times \frac{100^3 \cancel{\text{ cm}^3}}{\text{m}^3}$$

$$\rho = 998 \text{ kg m}^{-3}$$

a. For  $r = 1 \text{ mm} = 10^{-3} \text{ m}$ ,

$$h = \frac{2(7.27 \times 10^{-2} \text{ N m}^{-1})}{(998 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})(10^{-3} \text{ m})}$$

we know that  $1\text{N} = 1 \frac{\text{kg m}}{\text{s}^2}$

$$h = \frac{2\left(7.27 \times 10^{-2} \frac{\cancel{\text{kg}} \cancel{\text{m}}}{\cancel{\text{s}^2}} \cancel{\text{m}^{-1}}\right)}{(998 \cancel{\text{kg}} \text{ m}^{-3})(9.81 \text{ m } \cancel{\text{s}^{-2}})(10^{-3} \text{ m})}$$

$$h = 0.148 \ 513 \ 13 \text{ m}$$

$$\boxed{h = 1.49 \times 10^{-2} \text{ m or } 1.49 \text{ cm}}$$

- b. For  $r = 10^{-3} \text{ cm} = 10^{-5} \text{ m}$ ,

$$h = \frac{2(7.27 \times 10^{-2} \text{ N m}^{-1})}{(998 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})(10^{-5} \text{ m})}$$

$$h = 1.485 \ 131 \ 323 \text{ m}$$

$$\boxed{h = 1.49 \text{ m}}$$

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**18.18.** The density of liquid mercury at 273 K is  $13.6 \text{ g cm}^{-3}$  and the surface tension is  $0.47 \text{ N m}^{-1}$ . If the contact angle is  $140^\circ$ , calculate the capillary depression in a tube of 1-mm diameter.

**Solution:**

Given:  $T = 273 \text{ K}$ ,  $\rho = 13.6 \text{ g cm}^{-3}$ ,  $\gamma = 0.47 \text{ N m}^{-1}$ ,  $\theta = 140^\circ$ ,  $d = 1 \text{ mm}$

Required: capillary depression

From Eq. 18.55,

$$h = \frac{2\gamma \cos \theta}{\rho g r}$$

$$\rho = 13.6 \cancel{\text{ g}} \cancel{\text{ cm}^{-3}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{ g}}} \times \frac{100^3 \cancel{\text{ cm}^3}}{\text{m}^3}$$

$$\rho = 13\,600 \text{ kg m}^{-3}$$

$$r = \frac{d}{2} = \frac{10^{-3} \text{ m}}{2} = 5 \times 10^{-4} \text{ m}$$

$$h = \frac{2(0.47 \text{ N m}^{-1})\cos(140^\circ)}{(13\,600 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})(5 \times 10^{-4} \text{ m})}$$

$$h = -0.010\,794\,534 \text{ m}$$

$$\boxed{h = -10.8 \text{ mm}}$$

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**18.19.** The density of water at 20 °C is  $0.998 \text{ g cm}^{-3}$  and the surface tension is  $7.27 \times 10^{-2} \text{ N m}^{-1}$ . Calculate the ratio between the vapor pressure of a mist droplet having a mass of  $10^{-12} \text{ g}$  and the vapor pressure of water at a plane surface.

**Solution:**

Given:  $T = 20 \text{ }^{\circ}\text{C}$ ,  $\rho = 0.998 \text{ g cm}^{-3}$ ,  $\gamma = 7.27 \times 10^{-2} \text{ N m}^{-1}$ ,  $m = 10^{-12} \text{ g}$

Required: ratio between the vapor pressure of a mist droplet and of water

$$\text{Volume of droplet} = \frac{M}{\rho} = \frac{10^{-12} \cancel{\text{g}}}{0.998 \cancel{\text{g}} \text{ cm}^{-3}}$$

$$V = 1.002\,004\,008 \times 10^{-12} \text{ cm}^3$$

$$V = 1.002\,004\,008 \times 10^{-18} \text{ m}^3$$

$$V = \frac{4}{3} \pi r^3$$

$$r = \left( \frac{3V}{4\pi} \right)^{1/3}$$

$$r = \left[ \frac{3(1.002\,004\,008 \times 10^{-18} \text{ m}^3)}{4\pi} \right]^{1/3}$$

$$r = 6.207\,646\,102 \times 10^{-7} \text{ m}$$

$$\ln \frac{P}{P_0} = \frac{2\gamma M}{\rho r RT}$$

$$\ln \frac{P}{P_0} = \frac{2(7.27 \times 10^{-2} \text{ N m}^{-1})(18.02 \times 10^{-3} \text{ kg mol}^{-1})}{(998 \text{ kg m}^{-3})(6.207 \ 646 \ 102 \times 10^{-7} \text{ m})(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}$$

we know that  $1 \text{ N} = 1 \frac{\text{kg m}}{\text{s}^2}$  and  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$

$$\ln \frac{P}{P_0} = \frac{2\left(7.27 \times 10^{-2} \frac{\text{kg m}}{\text{s}^2} \text{ m}^{-1}\right)(18.02 \times 10^{-3})}{(998 \text{ m}^{-3})(6.207 \ 646 \ 102 \times 10^{-7} \text{ m})(8.3145 \text{ kg m}^2 \text{ s}^{-2})(298.15)}$$

$$\ln \frac{P}{P_0} = 1.706 \ 046 \ 055 \times 10^{-3}$$

$$\frac{P}{P_0} = \exp(1.706 \ 046 \ 055 \times 10^{-3})$$

$$\frac{P}{P_0} = 1.001 \ 707 \ 502$$

$$\boxed{\frac{P}{P_0} = 1.0017}$$

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**18.20.** The two arms of a U-tube have radii of 0.05 cm and 0.10 cm. A liquid of density  $0.80 \text{ g cm}^{-3}$  is placed in the tube, and the height in the narrower arm is found to be 2.20 cm higher than that in the wider arm. Calculate the surface tension of the liquid, assuming  $\theta = 0^\circ$ .

**Solution:**

Given:  $r_1 = 0.05 \text{ cm}$ ,  $r_2 = 0.10 \text{ cm}$ ,  $\rho = 0.80 \text{ g cm}^{-3}$ ,  $\Delta h = 2.20 \text{ cm}$ ,  $\theta = 0^\circ$

Required:  $\gamma$

From Eq. 18.54, the height is  $\frac{2\gamma}{r\rho g}$  and the difference in heights is

$$\Delta h = \frac{2\gamma}{\rho g} \left( \frac{1}{r_1} - \frac{1}{r_2} \right)$$

Thus

$$0.022 \text{ m} = \frac{2\gamma}{(0.80 \times 10^3 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})} \left( \frac{1}{5 \times 10^{-4} \text{ m}} - \frac{1}{10^{-3} \text{ m}} \right)$$

$$0.022 \text{ m} = \frac{2\gamma(2000 - 1000) \text{ m}^{-1}}{(0.80 \times 10^3 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})}$$

$$0.022 \text{ m} = (0.254 \ 841 \ 998 \text{ kg}^{-1} \text{ m s}^{-2}) \gamma$$

$$\gamma = 0.086 \ 328 \text{ kg s}^{-2}$$

$$\gamma = 0.086 \ 328 \text{ N m}^{-1}$$

$$\boxed{\gamma = 0.086 \text{ N m}^{-1}}$$

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**18.21.** A tube is placed in a certain liquid and the capillary rise is 1.5 cm. What would be the rise if the same tube were placed in another liquid that has half the surface tension and half the density of the first liquid? Assume that  $\theta = 0$  in both cases.

**Solution:**

Given: capillary rise = 1.5 cm,  $\theta = 0$ ,  $\gamma_2 = \frac{1}{2}\gamma_1$ ,  $\rho_2 = \frac{1}{2}\rho_1$

Required: capillary rise in new liquid

The rise is proportional to  $\frac{\gamma}{\rho}$  and is therefore the same in the second liquid, i.e., 1.5 cm.

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**18.22.** When a certain capillary tube is placed in water, the capillary rise is 2.0 cm. Suppose that the tube is placed in the water in such a way that only 1.0 cm is above the surface; will the water flow over the edge? Explain your answer.

**Solution:**

Given: capillary rise = 2.0 cm, 1.0 cm above surface

Required: Explanation

No, the water does not flow over the edge. The meniscus will rise to the top of the tube and then the radius of curvature will decrease until the capillary pressure just balances the pressure of the column of liquid; equilibrium is then established. This will occur when the radius of curvature at the surface is half what it is in a longer tube.

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**\*18.23.** A layer of benzene, of density  $0.8 \text{ g cm}^{-3}$ , is floating on water of density  $1.0 \text{ g cm}^{-3}$ , and a vertical tube of internal diameter  $0.1 \text{ mm}$  is inserted at the interface. It is observed that there is a capillary rise of  $4.0 \text{ cm}$  and that the contact angle is  $40^\circ$ . Calculate the interfacial tension between water and benzene.

**Solution:**

Given:  $\rho_{\text{benzene}} = 0.8 \text{ g cm}^{-3}$ ,  $\rho_{\text{water}} = 1.0 \text{ g cm}^{-3}$ ,  $d_i = 0.1 \text{ mm}$ ,  $h = 4.0 \text{ cm}$ ,  $\theta = 40^\circ$

Required:  $\gamma$

The equation that applies is an extension of Eq. 18.55:

$$\gamma = \frac{rh(\Delta\rho)g}{2\cos\theta}$$

where  $\Delta\rho$  is the difference between the two densities. Then

$$\gamma = \frac{\left[(1.00 - 0.80) \times 10^3 \text{ kg m}^{-3}\right] (9.81 \text{ m s}^{-2}) (0.040 \text{ m}) (0.5 \times 10^{-4} \text{ m})}{2\cos(40^\circ)}$$

$$\gamma = 2.561\,209\,102 \times 10^{-3} \text{ kg s}^{-2}$$

$$\boxed{\gamma = 2.56 \times 10^{-3} \text{ N m}^{-1}} \quad (\text{N} \equiv \text{kg m s}^{-2})$$

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**18.24.** A liter of water at 20 °C is broken up into a spray in which the droplets have an average radius of  $10^{-5}$  cm. If the surface tension of water at 20 °C is  $7.27 \times 10^{-2} \text{ N m}^{-1}$ , calculate the Gibbs energy change when the droplets are formed.

**Solution:**

Given:  $T = 20 \text{ }^{\circ}\text{C}$ ,  $V_{\text{water}} = 1 \text{ L}$ ,  $r_{\text{droplet}} = 10^{-5} \text{ cm}$ ,  $\gamma = 7.27 \times 10^{-2} \text{ N m}^{-1}$

Required: Gibbs energy change

The Gibbs energy change is the work done, which is the surface tension multiplied by the change in surface area (Eq. 18.50).

The surface area of the water in bulk can be estimated on the assumption that the liter of water was present as a sphere. The volume,  $1 \text{ dm}^3$ , is  $10^{-3} \text{ m}^3$ , and the radius  $r$  is

$$V = \frac{4}{3} r^3 \pi$$

$$r = \left( \frac{3V}{4\pi} \right)^{1/3}$$

$$r = \left( \frac{3 \times 10^{-3} \text{ m}^3}{4\pi} \right)^{1/3}$$

$$r = 0.062 \ 035 \ 049 \text{ m}$$

The surface area,  $4\pi r^2$ , is thus

$$4\pi \times (0.062 \ 035 \ 049 \text{ m})^2 = 0.048 \ 359 \ 758 \text{ m}^2$$

The surface area of each droplet is

$$4\pi \times (10^{-7} \text{ m})^2 = 1.256 \ 637 \ 061 \times 10^{-13} \text{ m}^2$$

here  $r$  is the average radius of each droplet, i.e.,  $10^{-5} \text{ cm}$

And the volume of each droplet is

$$\frac{4}{3}\pi \times (10^{-7} \text{ m})^3 = 4.188\,790\,205 \times 10^{-21} \text{ m}^3$$

The number of droplets is therefore the volume of water in bulk divided by the volume of each droplet

$$\frac{10^{-3} \text{ m}^3}{4.188\,790\,205 \times 10^{-21} \text{ m}^3} = 2.387\,324\,146 \times 10^{17} \text{ droplets}$$

Now that we know the number of droplets and the surface area for a single droplets, we can calculate the total surface area of the droplets:

$$(2.387\,324\,146 \times 10^{17}) (1.256\,637\,061 \times 10^{-13} \text{ m}^2) = 299\,99.999\,99 \text{ m}^2$$

This is effectively the increase in surface area, and the increase in Gibbs energy is

$$\text{Gibbs energy} = \gamma \times \text{surface area}$$

$$\text{Gibbs energy} = (7.27 \times 10^{-2} \text{ N m}^{-1}) (299\,99.999\,99 \text{ m}^2)$$

$$\text{Gibbs energy} = 2\,180.999\,999 \text{ J}$$

$$\boxed{\text{Gibbs energy} = 2.181 \text{ kJ}}$$

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**18.25.** Benjamin Franklin demonstrated on a number of occasions that a teaspoonful of oil put on water would produce a layer half an acre in area (1 acre = 4840 square yards; 1 yard = 0.915 m). Assume a teaspoonful to be  $1\text{ cm}^3$ , and estimate the thickness of the film.

**Solution:**

Given: see above

Required: estimation of the thickness of the film

An acre is 4840 square yards =  $4840 \times (0.915)^2\text{ m}^2 = 4052\text{ m}^2$ . Thus, half an acre is approximately  $2000\text{ m}^2$ . The thickness of the film is thus

$$\frac{10^{-6}\text{ m}^3}{2000\text{ m}^2} = 5 \times 10^{-10}\text{ m} = 5\text{ \AA}$$

This is a reasonable estimate, considering the approximate nature of the area and volume. Lord Rayleigh later estimated the thickness of an oil film to be about  $10\text{ \AA}$ , and similar values were obtained in Langmuir's work.

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**18.26.** A fatty acid was spread on the surface of water in a Langmuir film balance at 15 °C, and the following results obtained:

Area/cm <sup>2</sup> μg <sup>-1</sup>	5.7	28.2	507	1070	2200	11100
Surface pressure/ 10 <sup>-3</sup> N m <sup>-1</sup>	30	0.3	0.2	0.1	0.05	0.01

Estimate the molecular weight of the acid and the area per molecule when the film was fully compressed.

**Solution:**

Given:  $T = 15\text{ }^{\circ}\text{C}$ , above table

Required: molecular weight of the acid, area per molecule when film is fully compressed

At the three lower pressures,  $\pi A$  is constant within the experimental error and has a value of

$$1.11 \times 10^4 \text{ N m kg}^{-1} (= \text{J kg}^{-1})$$

$\pi A$  is equal to  $RT$  and therefore,

$$\pi A = 8.3145 \times 288.15 = 2395.823 \text{ J mol}^{-1}$$

The molar mass is thus

$$\frac{2395.823 \text{ J mol}^{-1}}{1.11 \times 10^4 \text{ J kg}^{-1}} = 0.215 \text{ kg mol}^{-1} = 215.839 \text{ g mol}^{-1}$$

$$\boxed{\text{MW} = 216 \text{ g mol}^{-1}}$$

At the highest pressure, i.e., when the film is fully compressed, the area is  $5.7 \text{ cm}^2 \mu\text{g}^{-1}$ . Since  $216 \text{ g} = 6.022 \times 10^{23}$  molecules,

$$1 \mu\text{g} = \frac{6.022 \times 10^{23} \times 10^{-6}}{216} = 2.787 \text{ } 962 \text{ } 963 \times 10^{15} \text{ molecules}$$

Thus, 1 molecule occupies

$$\text{area per molecule} = \frac{5.7 \text{ cm}^2 \cancel{\mu\text{g}^{-1}}}{2.787\,962\,963 \times 10^{15} \text{ molecule } \cancel{\mu\text{g}^{-1}}}$$

$$\text{area per molecule} = 2.044\,503\,487 \times 10^{-15} \text{ cm}^2 \text{ molecule}^{-1}$$

$$\text{area per molecule} = 0.204\,450\,348 \text{ nm}^2 \text{ molecule}^{-1}$$

$\text{area per molecule for fully compressed film} = 0.204 \text{ nm}^2 \text{ molecule}^{-1}$
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**18.27.** N. K. Adam carried out surface film studies using a Langmuir film balance 14.0 cm in width having a floating barrier 13.8 cm long. In one investigation he introduced 52.0  $\mu\text{g}$  of 1-hexadecanol ( $\text{C}_{16}\text{H}_{33}\text{OH}$ ) onto the surface and measured the force on the float at various lengths of the film, obtaining the following results:

Length/cm	Force on float/ $10^{-5}\text{ N}$
20.9	4.14
20.3	8.56
20.1	26.2
19.6	69.0
19.1	108.0
18.6	234
18.3	323
18.1	394
17.8	531

Estimate the area per molecule when the film was fully compressed.

**Solution:**

Given: see above

Required: estimate the area per molecule for fully compressed film.

The molecular weight of 1-hexadecanol is 242.43  $\text{g mol}^{-1}$ , and 52.0  $\mu\text{g}$  therefore contains

$$\frac{52.0 \cancel{\mu\text{g}}}{242.43 \cancel{\text{g}} \text{ mol}^{-1}} \times \frac{1 \cancel{\text{g}}}{10^6 \cancel{\mu\text{g}}} = 2.144\,949\,057 \times 10^{-7} \text{ mol}$$

We can start by constructing a table showing all

$$(2.144\,949\,057 \times 10^{-7} \text{ mol}) (6.022 \times 10^{23} \text{ molecules mol}^{-1}) = 1.291\,688\,322 \times 10^{17} \text{ molecules}$$

surface pressures and area per molecule

Length/cm	Area/cm <sup>2</sup>	Force/10 <sup>-5</sup> N	Surface Pressure/ 10 <sup>-4</sup> N m <sup>-1</sup>	Area per molecule/nm <sup>2</sup>
20.9	292.6	4.14	3.00	0.227
20.3	284.2	8.56	6.20	0.220
20.1	281.4	26.2	19.0	0.218
19.6	274.4	69.0	50.0	0.212
19.1	267.4	108	78.3	0.207
18.6	260.4	234	169.6	0.202
18.3	256.2	323	234.1	0.198
18.1	253.4	394	285.5	0.196
17.8	249.2	531	384.8	0.193

Here,

$$\text{Area} = \text{Length} \times \text{film width}$$

$$\text{Surface Pressure} = \text{Force} \times \text{length of floating barrier}$$

$$\text{Area per molecule} = \frac{\text{Area}}{\text{number of molecules (i.e. } 1.291\,688\,322 \times 10^{17} \text{ molecules)}}$$



Since we do not know if fully compressed corresponds to the largest surface pressure in the above table, we can plot a graph of Surface pressure vs. Area per molecule, and do extrapolation to find the value of area per molecule for fully compressed film.

[image]

From the graph, area that corresponds to fully compressed layer =  $0.19 \text{ nm}^2$ .

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CHAPTER

# 19

Transport Properties

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## Physical Chemistry

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# Problems and Solutions

**Chapter 19****Viscosity**

**19.1.** In a normal adult at rest the average speed of flow of blood through the aorta is  $0.33 \text{ m s}^{-1}$ . The radius of the aorta is 9 mm and the viscosity of blood at body temperature,  $37^\circ\text{C}$ , is about  $4.0 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ . Calculate the pressure drop along a 0.5 m length of the aorta.

[Solution](#)

- 19.2.** A typical human capillary is about 1 mm long and has a radius of  $2 \mu\text{m}$ . If the pressure drop along the capillary is 20 Torr,
- calculate the average linear speed of flow of blood of viscosity  $4.0 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ;
  - calculate the volume of blood passing through each capillary per second; and
  - estimate the number of capillaries in the body if they are supplied by the aorta described in Problem 19.1.

[Solution](#)

- \*19.3.** The viscosity of ethylene at  $25.0^\circ\text{C}$  and 101.325 kPa is  $9.33 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$ . Estimate
- the molecular diameter,
  - the mean free path,
  - the frequency of collisions  $Z_A$  experienced by a given molecule, and
  - the collision density  $Z_{AA}$ .

[Solution](#)

- \*19.4.** For nonassociated liquids the fluidity  $\phi$  (i.e., the reciprocal of the viscosity) obeys to a good approximation an equation of the Arrhenius form

$$\phi = Ae^{-E_a/RT}$$

where  $A$  and  $E_a$  are constants.

- a.** For liquid  $\text{CCl}_4$  the viscosity at  $0.0\text{ }^\circ\text{C}$  is  $1.33 \times 10^{-3}\text{ kg m}^{-1}\text{ s}^{-1}$  and the activation energy  $E_a$  is  $10.9\text{ kJ mol}^{-1}$ . Estimate the viscosity at  $40.0\text{ }^\circ\text{C}$ .
- b.** The Arrhenius equation does not apply well to associated liquids such as water, but it can be used over a limited temperature range. At  $20.0\text{ }^\circ\text{C}$  the viscosity of water is  $1.002 \times 10^{-3}\text{ kg m}^{-1}\text{ s}^{-1}$  and the activation energy for fluidity  $18.0\text{ kJ mol}^{-1}$ . Estimate the viscosity at  $40.0\text{ }^\circ\text{C}$ .

[Solution](#)

- 19.5.** At  $20.0\text{ }^\circ\text{C}$  the viscosity of pure toluene is  $5.90 \times 10^{-4}\text{ kg m}^{-1}\text{ s}^{-1}$ . Calculate the intrinsic viscosities of solutions containing  $0.1\text{ g dm}^{-3}$  of polymer in toluene and having the following viscosities:

- a.**  $5.95 \times 10^{-4}\text{ kg m}^{-1}\text{ s}^{-1}$
- b.**  $6.05 \times 10^{-4}\text{ kg m}^{-1}\text{ s}^{-1}$
- c.**  $6.27 \times 10^{-4}\text{ kg m}^{-1}\text{ s}^{-1}$

These solutions are sufficiently dilute that the reduced specific viscosity can be taken to be the intrinsic viscosity.

[Solution](#)

- \*19.6.** Suppose that solutions (a) and (c) in Problem 19.5 correspond to polymers of molecular weights 20 000 and 40 000, respectively. Assuming the Mark-Houwink equation 19.33 to apply, make an estimate of the molecular weight of the polymer in solution (b).

[Solution](#)

**19.7. a.** The activation energy for the fluidity of *n*-octane is  $12.6 \text{ kJ mol}^{-1}$  and the viscosity at  $0^\circ\text{C}$  is  $7.06 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ . Estimate the viscosity at  $40.0^\circ\text{C}$ , assuming the Arrhenius equation to apply.

**b.** A better temperature law for the viscosity of *n*-octane has been found to be

$$\eta = A(T/\text{K})^{-1.72} \exp(543/(T/\text{K}))$$

where  $T$  is expressed in kelvins.

Make another estimate of the viscosity at  $40^\circ\text{C}$ . What is the effective activation energy at  $20^\circ\text{C}$ ?

[Solution](#)

**\*19.8.** Over its entire liquid range the viscosity of water is represented to within 1% by the following empirical formula:

$$\ln\left(\frac{\eta(20^\circ\text{C})}{\eta(t^\circ\text{C})}\right) = \frac{3.1556(t - 20.0) + 1.925 \times 10^{-3}(t - 20.0)^2}{109.0 + t}$$

where  $t$  is the value of the temperature in degrees Celsius. Make a better estimate of the viscosity of water than obtained by the use of the Arrhenius equation (Problem 19.4b).

To what activation energies does this empirical expression correspond at

**a.**  $20^\circ\text{C}$ ?

**b.**  $100^\circ\text{C}$ ?

Give a qualitative explanation for the difference between the two values.

[Solution](#)

**\*19.9.** Consider a hypothetical gas in which the molecules have mass but no size and do not interact with each other.

**a.** What would be the viscosity of such a gas?

**b.** Suppose instead that the molecules have zero size but attract one another. What can you then say about the viscosity?

**c.** If they repel one another, what would the viscosity be?

**d.** Give a clear explanation of your conclusions in all three cases.

[Solution](#)

**Diffusion**

**19.10.** The molecular diameter of the helium atom is 0.225 nm. Estimate, at 0 °C and 101.325 kPa,

- a. the viscosity of the gas,
- b. the self-diffusion coefficient,
- c. the mean speed of the molecules,
- d. the mean free path,
- e. the collision frequency  $Z_A$ , and
- f. the collision density  $Z_{AA}$ .

[Solution](#)

**19.11.** Calculate the mean square distance traveled by a molecule of  $H_2$  at 20 °C and 101.325 kPa in 10 s ( $D = 1.005 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ ).

[Solution](#)

**19.12.** Solutions of (a) glucose ( $D = 6.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) and (b) tobacco mosaic virus ( $D = 5.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ) were maintained at a constant temperature of 20 °C and without agitation for 100 days. How far would a given molecule of each be expected to diffuse in that time?

[Solution](#)

**19.13.** Estimate the diffusion coefficient of cupric sulfate in water at 25 °C from the molar conductivities given in Table 7.3 (p. 291).

[Solution](#)

**19.14.** Estimate the diffusion coefficient of sodium acetate in water at 25 °C from the following mobility values:

$\text{Na}^+$ :	$5.19 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
$\text{CH}_3\text{COO}^-$ :	$4.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

[Solution](#)

**19.15.** The diffusion coefficient for horse hemoglobin in water is  $6.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  at  $20^\circ \text{C}$ . The viscosity of water at  $20^\circ \text{C}$  is  $1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$  and the specific volume of the protein is  $0.75 \text{ cm}^3 \text{ g}^{-1}$ . Assume the hemoglobin molecule to be spherical and to obey Stokes's law, and estimate its radius and the molecular weight.

[Solution](#)

**19.16.** If the diffusion coefficient for insulin is  $8.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  at  $20^\circ \text{C}$ , estimate the mean time required for an insulin molecule to diffuse through a distance equal to the diameter of a typical living cell ( $\approx 10 \mu\text{m}$ ).

[Solution](#)

**\*19.17.** A colloidal particle is spherical and has a diameter of  $0.3 \mu\text{m}$  and a density of  $1.18 \text{ g cm}^{-3}$ . Estimate how long it will take for the particle to diffuse through a distance of  $1 \text{ mm}$  in water at  $20^\circ \text{C}$  ( $\eta = 1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ; the density of water at  $20^\circ \text{C} = 0.998 \text{ g cm}^{-3}$ ). (See also Problem 19.21.)

[Solution](#)

### Sedimentation and Diffusion

**19.18.** Diphtheria toxin was found to have, at  $20^\circ \text{C}$ , a sedimentation coefficient of  $4.60$  Svedbergs and a diffusion coefficient of  $5.96 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . The toxin has a specific volume of  $0.736 \text{ cm}^3 \text{ g}^{-1}$ , and the density of water at  $20^\circ \text{C}$  is  $0.998 \text{ g cm}^{-3}$ . Estimate a value for the molecular weight of the toxin.

[Solution](#)

**19.19.** A protein has a sedimentation coefficient of  $1.13 \times 10^{-12} \text{ s}^{-1}$  at  $25^\circ \text{C}$  and a diffusion coefficient of  $4.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The density of the protein is  $1.32 \text{ g cm}^{-3}$  and that of water at  $25^\circ \text{C}$  is  $0.997 \text{ g cm}^{-3}$ . Calculate the molecular weight of the protein.

[Solution](#)

**\*19.20.** A protein of molecular weight  $60\,000$  has a density of  $1.31 \text{ g cm}^{-3}$  and in water at  $25^\circ \text{C}$  ( $\rho = 0.997 \text{ g cm}^{-3}$ ;  $\eta = 8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ ) it has a sedimentation coefficient of  $4.1 \times 10^{-13} \text{ s}^{-1}$ . Calculate the frictional coefficient  $f$

a. from the sedimentation coefficient, and

b. by the use of Stokes's law.

Suggest a reason why the two values are not quite the same.

[Solution](#)

**\*19.21.** How long will it take the particle from Problem 19.17 to sediment a distance of 1 mm in the earth's gravitational field ( $g = 9.81 \text{ m s}^{-2}$ )?

[Solution](#)

**\*19.22.** An aqueous colloidal solution contains spherical particles of uniform size and of density  $1.33 \text{ g cm}^{-3}$ . The diffusion coefficient at  $25^\circ\text{C}$  is  $1.20 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ; make an estimate of the sedimentation coefficient ( $\rho(\text{H}_2\text{O}) = 0.997 \text{ g cm}^{-3}$ ;  $\eta(\text{H}_2\text{O}) = 8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ ).

[Solution](#)

**19.23.** At  $20^\circ\text{C}$ ,  $\gamma$ -globulin has a sedimentation constant of  $7.75 \times 10^{-13} \text{ s}$ , a diffusion coefficient in water of  $4.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , and a density of  $1.353 \text{ g cm}^{-3}$ . The density of water at  $20^\circ\text{C}$  is  $0.998 \text{ g cm}^{-3}$ .

**a.** Estimate the molecular weight of  $\gamma$ -globulin.

**b.** Assuming the Stokes-Einstein equation to apply, estimate the radius of the protein molecule. The viscosity of water at  $20^\circ\text{C}$  is  $1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ .

[Solution](#)

**\*19.24.** A sample of human hemoglobin had a sedimentation constant of 4.48 Svedbergs in water at  $20^\circ\text{C}$  and a diffusion coefficient of  $6.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The specific volume of human hemoglobin is  $0.749 \text{ cm}^3 \text{ g}^{-1}$ , and the density of water at  $20^\circ\text{C}$  is  $0.998 \text{ g cm}^{-3}$ .

**a.** Estimate the molecular weight of human hemoglobin.

**b.** How far would a molecule diffuse in 1 minute?

**c.** Neglect diffusion and estimate how far a molecule would sediment in 1 minute.

**d.** In a centrifuge rotating at 15 000 rpm, how far would a molecule sediment in 1 minute if it were 20 cm from the center of rotation?

**e.** Assume the molecule to be spherical and estimate its radius by the use of the Stokes-Einstein equation.

**f.** Estimate the radius from the molecular weight and the density.

[Solution](#)



**\*19.25.** In the first decade of the twentieth century Jean Perrin carried out important investigations on the sedimentation, in the gravitational field, of particles of gamboge, mastic, and other paint pigments. Consider particles of density  $1.2 \text{ g cm}^{-3}$  and of the following radii:

- a. 1 mm
- b. 0.1 mm
- c.  $10 \mu\text{m}$
- d.  $1 \mu\text{m}$
- e. 10 nm

In each case, assuming Stokes's law to apply, estimate the distance the particle would sediment in 1 hour, in water at  $20^\circ\text{C}$  (viscosity,  $\eta = 1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$  and density  $0.998 \text{ g cm}^{-3}$ ).

f. In the case of the particle having a radius of 10 nm, what speed of rotation in an ultracentrifuge would be required to bring about a sedimentation of 1 mm in 1 hour? Take the distance from the axis of rotation to be 10 cm.

[Solution](#)

**\*19.26.** Perrin also carried out, using pigment particles, experiments on Brownian movement in which he determined distances traveled by individual particles in various periods of time. For each of the particles of five different radii mentioned in the previous problem, estimate the diffusion coefficient and the average distance traveled in 1 hour. Take the water temperature again as  $20^\circ\text{C}$  and use the data of Problem 19.25.

[Solution](#)

**\*19.27.** A pure protein in water is centrifuged to equilibrium at  $25^\circ\text{C}$  and at 25 000 rpm. At distances of 8.34 cm and 9.12 cm from the axis of rotation the concentrations of the protein are measured to be  $3.52 \text{ g cm}^{-3}$  and  $22.49 \text{ g cm}^{-3}$ , respectively. The specific volume  $V_1$  of the protein is  $0.78 \text{ cm}^3 \text{ g}^{-1}$ , and the density of water at  $25^\circ\text{C}$  is  $0.997 \text{ g cm}^{-3}$ . Calculate the molecular weight of the protein.

[Solution](#)

**\*19.28.** A protein has a molecular weight of 1 000 000 and a specific volume of  $0.81 \text{ cm}^3 \text{ g}^{-1}$ . In an ultracentrifuge at  $25^\circ\text{C}$ , what speed of revolution is required to produce at equilibrium a concentration ratio of 20/1 at distances 10.00 cm and 9.00 cm from the axis of revolution? The density of water at  $25^\circ\text{C}$  is  $0.997 \text{ g cm}^{-3}$ .

[Solution](#)

**Essay Questions**

**19.29.** Explain how the rate of diffusion through a membrane depends on

- a. the size of the diffusing substance, and
- b. its solubility in the membrane.

**19.30.** Explain clearly the different mechanisms involved in the viscosity of gases and the viscosity of liquids.

**Solutions**

**19.1.** In a normal adult at rest the average speed of flow of blood through the aorta is  $0.33 \text{ m s}^{-1}$ . The radius of the aorta is 9 mm and the viscosity of blood at body temperature,  $37^\circ\text{C}$ , is about  $4.0 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ . Calculate the pressure drop along a 0.5 m length of the aorta.

**Solution:**

Given:  $v_{\text{blood}} = 0.33 \text{ m s}^{-1}$ ,  $r_{\text{aorta}} = 9 \text{ mm}$ ,  $\eta = 4.0 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ,  $l = 0.5 \text{ m}$

Required:  $\Delta P$

To solve this problem we will use Eq. 19.10, the Poiseuille Equation.

$$\frac{dV}{dt} = \frac{(P_1 - P_2) \pi R^4}{8 \eta l}$$

Rearranging for  $\Delta P$  we get,

$$\Delta P = \frac{8 \eta l}{\pi R^4} \cdot \frac{dV}{dt}$$

To find the volume rate of flow, we find the area of the cross section of the aorta and multiply by the rate of blood flow through the aorta.

$$\frac{dV}{dt} = A \times v_{\text{blood}}$$

$$A = \pi r_{\text{aorta}}^2$$

$$\frac{dV}{dt} = \pi r_{\text{aorta}}^2 v_{\text{blood}}$$

$$\frac{dV}{dt} = \pi (9 \times 10^{-3} \text{ m})^2 (0.33 \text{ m s}^{-1})$$

$$\frac{dV}{dt} = 8.39748 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$$

Solving for  $\Delta P$  we get,

$$\Delta P = \frac{8(4.0 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})(0.5 \text{ m})}{\pi(9 \times 10^{-3} \text{ m})^4} (8.39748 \times 10^{-5} \text{ m}^3 \text{ s}^{-1})$$

$$\Delta P = 65.18518519 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$1 \text{ kg m}^{-1} \text{ s}^{-2} = 1 \text{ Pa}$$

$$\boxed{\Delta P = 65 \text{ Pa}}$$

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- 19.2.** A typical human capillary is about 1 mm long and has a radius of  $2\ \mu\text{m}$ . If the pressure drop along the capillary is 20 Torr,
- calculate the average linear speed of flow of blood of viscosity  $4.0 \times 10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}$ ;
  - calculate the volume of blood passing through each capillary per second; and
  - estimate the number of capillaries in the body if they are supplied by the aorta described in Problem 19.1.

**Solution:**

Given:  $l = 1\ \text{mm}$ ,  $r = 2\ \mu\text{m}$ ,  $\Delta P = 20\ \text{Torr}$ ,  $\eta = 4.0 \times 10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}$

Required:  $v_{\text{blood}}$ ,  $\frac{dV}{dt}$ , number of capillaries

- a. To calculate the average linear speed of blood flow, we use Eq. 19.10,

$$\frac{dV}{dt} = \frac{(P_1 - P_2)\pi R^4}{8\eta l}$$

The volume rate of flow is found from the area of the cross section of the aorta multiplied by the rate of blood flow through the aorta.

$$\frac{dV}{dt} = A \times v_{\text{blood}}$$

$$A = \pi r_{\text{aorta}}^2$$

$$\frac{dV}{dt} = \pi r_{\text{aorta}}^2 v_{\text{blood}}$$

Rearranging to solve for  $v_{\text{blood}}$  we obtain,

$$\pi r_{\text{aorta}}^2 v_{\text{blood}} = \frac{\Delta P \pi R^4}{8 \eta l}$$

$$v_{\text{blood}} = \frac{\cancel{\Delta P} \cancel{\pi} R^4}{8 \eta l \cancel{\pi} r_{\text{aorta}}^2}$$

$$R = r_{\text{aorta}}$$

$$v_{\text{blood}} = \frac{\Delta P R^2}{8 \eta l}$$

$$\Delta P = 20 \cancel{\text{Torr}} \times 133.3 \frac{\text{Pa}}{\cancel{\text{Torr}}}$$

$$1 \text{ kg m}^{-1} \text{ s}^{-2} = 1 \text{ Pa}$$

$$v_{\text{blood}} = \frac{(20 \times 133.3 \text{ kg m}^{-1} \text{ s}^{-2})(2 \times 10^{-6} \text{ m})^2}{8(4.0 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})(1 \times 10^{-3} \text{ m})}$$

$$v_{\text{blood}} = 3.3325 \times 10^{-4} \text{ m s}^{-1}$$

$$\boxed{v_{\text{blood}} = 3.3 \times 10^{-4} \text{ m s}^{-1}}$$

b. The volume of blood flow is defined above as,

$$\frac{dV}{dt} = \pi r_{\text{aorta}}^2 v_{\text{blood}}$$

$$\frac{dV}{dt} = \pi (2 \times 10^{-6} \text{ m})^2 (3.3325 \times 10^{-4} \text{ m s}^{-1})$$

$$\frac{dV}{dt} = 4.18774 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$$

$$\boxed{\frac{dV}{dt} = 4.2 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}}$$

c. To calculate the number of capillaries, we divide the volume of flow through the aorta (from Problem 19.1) by the volume of flow through the capillaries.

$$\text{Number of capillaries} = \frac{dV_{\text{aorta}}}{dt} \div \frac{dV_{\text{capillaries}}}{dt}$$

$$\text{Number of capillaries} = \frac{8.397\,48 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}}{4.187\,74 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}}$$

$$\text{Number of capillaries} = 20\,052\,513\,128$$

$$\boxed{\text{Number of capillaries} = 2.0 \times 10^{10}}$$

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**\*19.3.** The viscosity of ethylene at 25.0 °C and 101.325 kPa is  $9.33 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$ . Estimate

- a. the molecular diameter,
- b. the mean free path,
- c. the frequency of collisions  $Z_A$  experienced by a given molecule, and
- d. the collision density  $Z_{AA}$ .

**Solution:**

Given:  $T = 25.0 \text{ °C}$ ,  $P = 101.325 \text{ kPa}$ ,  $\eta = 9.33 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$

Required:  $d$ ,  $\lambda$ ,  $Z_A$ ,  $Z_{AA}$

- a. The molecular diameter is given in Eq. 19.15 as,

$$\eta = \frac{m\bar{u}}{2\sqrt{2}\pi d^2}$$

And therefore  $d$  is,

$$d = \sqrt{\frac{m\bar{u}}{2\sqrt{2}\pi\eta}}$$

We calculate  $\bar{u}$  from Table 1.3 as,



$$\bar{u} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}$$

$$m = \frac{M}{N_{\text{A}}}$$

$$M = 2(12.011 \text{ g mol}^{-1}) + 4(1.00794 \text{ g mol}^{-1})$$

$$M = 28.05376 \text{ g mol}^{-1}$$

$$m = \frac{28.05376 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times 10^{-3}$$

$$m = 4.65855 \times 10^{-26} \text{ kg}$$

$$\bar{u} = \sqrt{\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}{\pi(4.65855 \times 10^{-26} \text{ kg})}}$$

$$\bar{u} = 474.4157955 \text{ m s}^{-1}$$

Solving for the diameter, we obtain

$$d = \sqrt{\frac{(4.65855 \times 10^{-26} \text{ kg})(474.4157955 \text{ m s}^{-1})}{2\sqrt{2}\pi(9.33 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1})}}$$

$$d = 5.16317 \times 10^{-10} \text{ m}$$

$$\boxed{d = 5.16 \times 10^{-10} \text{ m}}$$

b. The mean free path is given in Chapter 1 by Eq. 1.68

$$\lambda = \frac{V}{\sqrt{2}\pi d_{\text{A}}^2 N_{\text{A}}}$$

From the ideal gas law,

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} = \frac{101\,325\text{ Pa}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15)}$$

$$\frac{n}{V} = 40.873\,860\,75\text{ mol m}^{-3}$$

$$\frac{N}{V} = 40.873\,860\,75\text{ mol m}^{-3} \times 6.022 \times 10^{23}\text{ mol}^{-1}$$

$$\frac{N}{V} = 2.461\,42 \times 10^{25}\text{ m}^{-3}$$

Therefore the mean free path is,

$$\lambda = \frac{1}{\sqrt{2}\pi(5.163\,17 \times 10^{-10}\text{ m})^2(2.461\,42 \times 10^{25}\text{ m}^{-3})}$$

$$\lambda = 3.430\,17 \times 10^{-8}\text{ m}$$

$$\boxed{\lambda = 3.43 \times 10^{-8}\text{ m}}$$

c. The expression for  $Z_A$  is also found in Chapter 1 as Eq. 1.66,

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A}{V} \quad (\text{SI unit : s}^{-1})$$

Which we recognize as,

$$Z_A = \frac{\bar{u}_A}{\lambda}$$

$$Z_A = \frac{474.415\,795\,5\text{ m s}^{-1}}{3.430\,17 \times 10^{-8}\text{ m}}$$

$$Z_A = 13\,830\,675\,103\text{ s}^{-1}$$

$$\boxed{Z_A = 1.38 \times 10^{10}\text{ s}^{-1}}$$

d. From Eqs. 1.59 and 1.61,

$$Z_{AA} = \frac{1}{2} Z_A \frac{N}{V}$$

$$Z_{AA} = \frac{1}{2} (13\,830\,675\,103\,\text{s}^{-1}) (2.461\,42 \times 10^{25}\,\text{m}^{-3})$$

$$Z_{AA} = 1.702\,16 \times 10^{35}\,\text{m}^{-3}\,\text{s}^{-1}$$

$$\boxed{Z_{AA} = 1.70 \times 10^{35}\,\text{m}^{-3}\,\text{s}^{-1}}$$

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**\*19.4.** For nonassociated liquids the fluidity  $\phi$  (i.e., the reciprocal of the viscosity) obeys to a good approximation an equation of the Arrhenius form

$$\phi = Ae^{-E_a/RT}$$

where  $A$  and  $E_a$  are constants.

**a.** For liquid  $\text{CCl}_4$  the viscosity at  $0.0\text{ }^\circ\text{C}$  is  $1.33 \times 10^{-3}\text{ kg m}^{-1}\text{ s}^{-1}$  and the activation energy  $E_a$  is  $10.9\text{ kJ mol}^{-1}$ . Estimate the viscosity at  $40.0\text{ }^\circ\text{C}$ .

**b.** The Arrhenius equation does not apply well to associated liquids such as water, but it can be used over a limited temperature range. At  $20.0\text{ }^\circ\text{C}$  the viscosity of water is  $1.002 \times 10^{-3}\text{ kg m}^{-1}\text{ s}^{-1}$  and the activation energy for fluidity  $18.0\text{ kJ mol}^{-1}$ . Estimate the viscosity at  $40.0\text{ }^\circ\text{C}$ .

**Solution:**

Given:  $\text{CCl}_4$  :  $\eta_{0.0\text{ }^\circ\text{C}} = 1.33 \times 10^{-3}\text{ kg m}^{-1}\text{ s}^{-1}$ ,  $E_a = 10.9\text{ kJ mol}^{-1}$ ,  $T = 40.0\text{ }^\circ\text{C}$

$$T = 20.0\text{ }^\circ\text{C}, \eta = 1.002 \times 10^{-3}\text{ kg m}^{-1}\text{ s}^{-1}$$

Required:  $\eta_{40.0\text{ }^\circ\text{C}}$ , for  $\text{CCl}_4$  and water

**a.** Since  $A$  is a constant, we first calculate  $e^{-E_a/RT}$  at each temperature,

$$T = 0.0\text{ }^\circ\text{C}$$

$$\exp\left(\frac{-E_a}{RT}\right) = \exp\left(\frac{-10.9 \times 10^3\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1} \times 273.15\text{ K}}\right)$$

$$\exp\left(\frac{-E_a}{RT}\right) = 8.234\,485\,424 \times 10^{-3}$$

$$T = 40.0\text{ }^\circ\text{C}$$

$$\exp\left(\frac{-E_a}{RT}\right) = \exp\left(\frac{-10.9 \times 10^3\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1} \times 313.15\text{ K}}\right)$$

$$\exp\left(\frac{-E_a}{RT}\right) = 1.520\,131\,7 \times 10^{-2}$$

Since we are told viscosity has the inverse relationship to the fluidity  $\phi$ , we calculate the viscosity at 40.0 °C as,

$$\eta_{40.0^\circ\text{C}} = \eta_{0.0^\circ\text{C}} \times \frac{8.234\,485 \times 10^{-3}}{1.520\,131\,7 \times 10^{-2}}$$

$$\eta_{40.0^\circ\text{C}} = 1.33 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} \times \frac{8.234\,485 \times 10^{-3}}{1.520\,131\,7 \times 10^{-2}}$$

$$\eta_{40.0^\circ\text{C}} = 7.204\,55 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\boxed{\eta_{40.0^\circ\text{C}} = 7.20 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

b. Repeating the same procedure above for water, we get,

$$T = 20.0\text{ }^{\circ}\text{C}$$

$$\exp\left(\frac{-E_a}{RT}\right) = \exp\left(\frac{-18 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 293.15 \text{ K}}\right)$$

$$\exp\left(\frac{-E_a}{RT}\right) = 6.205\,331\,937 \times 10^{-4}$$

$$T = 40.0\text{ }^{\circ}\text{C}$$

$$\exp\left(\frac{-E_a}{RT}\right) = \exp\left(\frac{-18 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 313.15 \text{ K}}\right)$$

$$\exp\left(\frac{-E_a}{RT}\right) = 9.944\,936\,073 \times 10^{-4}$$

$$\eta_{40.0^{\circ}\text{C}} = \eta_{20.0^{\circ}\text{C}} \times \frac{6.205\,331\,937 \times 10^{-4}}{9.944\,936\,073 \times 10^{-4}}$$

$$\eta_{40.0^{\circ}\text{C}} = 1.002 \times 10^{-3} \times \frac{6.205\,331\,937 \times 10^{-4}}{9.944\,936\,073 \times 10^{-4}} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\eta_{40.0^{\circ}\text{C}} = 6.252\,169\,501 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\boxed{\eta_{40.0^{\circ}\text{C}} = 6.25 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

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**19.5.** At 20.0 °C the viscosity of pure toluene is  $5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ . Calculate the intrinsic viscosities of solutions containing  $0.1 \text{ g dm}^{-3}$  of polymer in toluene and having the following viscosities:

a.  $5.95 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

b.  $6.05 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

c.  $6.27 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

These solutions are sufficiently dilute that the reduced specific viscosity can be taken to be the intrinsic viscosity.

**Solution:**

Given:  $T = 20.0 \text{ °C}$ ,  $\eta_{\text{pure}} = 5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ ,  $\rho = 0.1 \text{ g dm}^{-3}$

Required:  $[\eta]$

Since we are told that the reduced specific viscosity can be taken to be the intrinsic viscosity, we solve using Eq. 19.31,

$$\text{reduced specific viscosity} = \frac{1}{\rho} \cdot \frac{\eta - \eta_0}{\eta_0} \equiv [\eta]$$

a.

$$[\eta] = \frac{1}{0.10 \text{ g dm}^{-3}} \cdot \frac{5.95 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1} - 5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}{5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

$$[\eta] = 0.084\,745\,763 \text{ dm}^3 \text{ g}^{-1}$$

$$[\eta] = 8.5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$$

b.

$$[\eta] = \frac{1}{0.10 \text{ g dm}^{-3}} \cdot \frac{6.05 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1} - 5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}{5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

$$[\eta] = 0.254\,237\,288 \text{ dm}^3 \text{ g}^{-1}$$

$$[\eta] = 0.25 \text{ m}^3 \text{ kg}^{-1}$$

c.

$$[\eta] = \frac{1}{0.10 \text{ g dm}^{-3}} \cdot \frac{6.27 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1} - 5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}{5.90 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

$$[\eta] = 0.627118644 \text{ dm}^3 \text{ g}^{-1}$$

$$\boxed{[\eta] = 0.63 \text{ m}^3 \text{ kg}^{-1}}$$

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**\*19.6.** Suppose that solutions (a) and (c) in Problem 19.5 correspond to polymers of molecular weights 20 000 and 40 000, respectively. Assuming the Mark-Houwink equation 19.33 to apply, make an estimate of the molecular weight of the polymer in solution (b).

**Solution:**

Given: Problem 19.5,  $M_a = 20\,000\text{ g mol}^{-1}$ ,  $M_c = 40\,000\text{ g mol}^{-1}$ , Eq.19.33

Required:  $M_b$

The Mark-Houwink equation, given by Eq.19.33 is

$$[\eta] = kM_r^\alpha$$

If it is obeyed, a plot of  $\log [\eta]$  against  $\log M_r$  will be a straight line.

Taking the logarithms of the solutions to Problem 19.5 gives,

$$\log [\eta_a] = \log (0.084\,745\,763)$$

$$\log [\eta_a] = -1.071\,882\,007$$

$$\log [\eta_b] = \log (0.254\,237\,288)$$

$$\log [\eta_b] = -0.594\,760\,753$$

$$\log [\eta_c] = \log (0.627\,118\,644)$$

$$\log [\eta_c] = -0.202\,650\,288$$

The logarithms of the molar masses,

$$\log M_a = \log (20\,000)$$

$$\log M_a = 4.301\,029\,996$$

$$\log M_c = \log (40\,000)$$

$$\log M_c = 4.602\,059\,991$$

Since we assume a linear relationship the slope will be,

$$m = \frac{\log[\eta_c] - \log[\eta_a]}{\log[M_c] - \log[M_a]}$$
$$m = \frac{-0.202\ 650\ 228 - (-1.071\ 882\ 007)}{4.602\ 059\ 991 - 4.301\ 029\ 996}$$
$$m = 2.887\ 525\ 474$$

Using  $y = mx + b$ , we can use the coordinate of  $\log M_a$  and  $\log[\eta_a]$  to determine the intercept  $b$ .

$$\log[\eta_a] = m \times \log M_a + b$$
$$-1.071\ 882\ 007 = 4.301\ 029\ 996 \times 2.887\ 525\ 474 + b$$
$$b = -13.491\ 212\ 568$$

the molar mass will then be,

$$\log[\eta_b] = m \times \log M_b + b$$
$$-0.594\ 760\ 753 = 2.887\ 525\ 474 \times M_b + (-13.491\ 212\ 568)$$
$$\log M_b = 4.466\ 264\ 254$$
$$M_b = 10^{4.466\ 264\ 254}$$
$$M_b = 29\ 259.321\ 7\ \text{g mol}^{-1}$$

$M_b = 2.9 \times 10^4\ \text{g mol}^{-1}$

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**19.7. a.** The activation energy for the fluidity of *n*-octane is  $12.6 \text{ kJ mol}^{-1}$  and the viscosity at  $0^\circ\text{C}$  is  $7.06 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ . Estimate the viscosity at  $40.0^\circ\text{C}$ , assuming the Arrhenius equation to apply.

**b.** A better temperature law for the viscosity of *n*-octane has been found to be

$$\eta = A(T/\text{K})^{-1.72} \exp(543/(T/\text{K}))$$

where  $T$  is expressed in kelvins.

Make another estimate of the viscosity at  $40^\circ\text{C}$ . What is the effective activation energy at  $20^\circ\text{C}$ ?

**Solution:**

Given:  $E_a = 12.6 \text{ kJ mol}^{-1}$ ,  $\eta_{0.0^\circ\text{C}} = 7.06 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

Required:  $\eta_{40.0^\circ\text{C}}$  using the Arrhenius equation and the equation above,  $E_a$

a. To solve this problem, we use the same procedure using in Problem 19.4.

$$T = 0.0\text{ }^{\circ}\text{C}$$

$$\exp(-E_a / RT) = \exp\left(\frac{-12.6 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}\right)$$

$$\exp(-E_a / RT) = 3.895\,402 \times 10^{-3}$$

$$T = 40.0\text{ }^{\circ}\text{C}$$

$$\exp(-E_a / RT) = \exp\left(\frac{-12.6 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(313.15 \text{ K})}\right)$$

$$\exp(-E_a / RT) = 7.912\,639\,816 \times 10^{-3}$$

$$\eta_{40.0\text{ }^{\circ}\text{C}} = \eta_{0.0\text{ }^{\circ}\text{C}} \times \frac{3.895\,402 \times 10^{-3}}{7.912\,639\,816 \times 10^{-3}}$$

$$\eta_{40.0\text{ }^{\circ}\text{C}} = (7.06 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}) \times \left(\frac{3.895\,402 \times 10^{-3}}{7.912\,639\,816 \times 10^{-3}}\right)$$

$$\eta_{40.0\text{ }^{\circ}\text{C}} = 3.475\,646\,404 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\boxed{\eta_{40.0\text{ }^{\circ}\text{C}} = 3.48 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

- b. Using the equation above, we get a better estimate.

$$\eta = A(T / \text{K})^{-1.72} \exp[543(T / \text{K})]$$

$$T = 0.0\text{ }^{\circ}\text{C}$$

$$T^{-1.72} \exp(543 / T) = (273.15)^{-1.72} \times \exp\left(\frac{543}{273.15}\right)$$

$$T^{-1.72} \exp(543/T) = 4.706\,868\,453 \times 10^{-4}$$

$$T = 40.0\text{ }^{\circ}\text{C}$$

$$T^{-1.72} \exp(543/T) = (313.15)^{-1.72} \times \exp\left(\frac{543}{313.15}\right)$$

$$T^{-1.72} \exp(543/T) = 2.886\,486\,719 \times 10^{-4}$$

$$\eta_{40.0\text{ }^{\circ}\text{C}} = \eta_{0.0\text{ }^{\circ}\text{C}} \times \frac{2.886\,486\,719 \times 10^{-4}}{4.706\,868\,453 \times 10^{-4}}$$

$$\eta_{40.0\text{ }^{\circ}\text{C}} = (7.06 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}) \times \left( \frac{2.886\,486\,719 \times 10^{-4}}{4.706\,868\,453 \times 10^{-4}} \right)$$

$$\eta_{40.0\text{ }^{\circ}\text{C}} = 4.329\,544\,461 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\boxed{\eta_{40.0\text{ }^{\circ}\text{C}} = 4.33 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

To calculate the activation energy we use the fluidity. The fluidity can be expressed as,

$$\phi = \frac{1}{\eta} = A^{-1} (T/\text{K})^{1.72} \exp\left(\frac{-4515 \text{ J mol}^{-1}}{RT}\right)$$

The activation energy at 20 °C is, by definition,

$$E_a = RT^2 \frac{d \ln \phi}{dT}$$

$$\ln \phi = 1.72 \ln(T / \text{K}) - \frac{4515 \text{ J mol}^{-1}}{RT}$$

$$\frac{d \ln \phi}{dT} = \frac{1.72}{T} + \frac{4515 \text{ J mol}^{-1}}{RT^2}$$

$$\frac{d \ln \phi}{dT} = \frac{1.72RT + 4515 \text{ J mol}^{-1}}{RT^2}$$

$$E_a = \cancel{RT^2} \left( \frac{1.72RT + 4515 \text{ J mol}^{-1}}{\cancel{RT^2}} \right)$$

$$E_a = 1.72 \left( 8.3145 \text{ J } \cancel{\text{K}^{-1}} \text{ mol}^{-1} \right) (293.15 \text{ } \cancel{\text{K}}) + 4515 \text{ J mol}^{-1}$$

$$E_a = 8707.320 \text{ J mol}^{-1}$$

$$\boxed{E_a = 8.71 \text{ kJ mol}^{-1}}$$

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**\*19.8.** Over its entire liquid range the viscosity of water is represented to within 1% by the following empirical formula:

$$\ln\left(\frac{\eta(20^\circ\text{C})}{\eta(t^\circ\text{C})}\right) = \frac{3.1556(t - 20.0) + 1.925 \times 10^{-3}(t - 20.0)^2}{109.0 + t}$$

where  $t$  is the value of the temperature in degrees Celsius. Make a better estimate of the viscosity of water than obtained by the use of the Arrhenius equation (Problem 19.4b).

To what activation energies does this empirical expression correspond at

**a.**  $20^\circ\text{C}$ ?

**b.**  $100^\circ\text{C}$ ?

Give a qualitative explanation for the difference between the two values.

**Solution:**

Given: empirical formula,  $T = 20^\circ\text{C}$ ,  $T = 100^\circ\text{C}$

Required:  $\eta_{\text{water}}$ ,  $E_a$

In problem 19.4b, we make an estimate at  $T = 40.0^\circ\text{C}$ . We are also given,  $\eta_{20^\circ\text{C}} = 1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$  Using the empirical formula, our improved estimate is,

$$\ln\left(\frac{\eta(20^\circ\text{C})}{\eta(40^\circ\text{C})}\right) = \frac{3.1556(40-20.0) + 1.925 \times 10^{-3}(40-20.0)^2}{109.0 + 40}$$

$$\ln(1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) - \ln \eta_{40^\circ\text{C}} = \frac{3.1556(20.0) + 1.925 \times 10^{-3}(400)}{149.0}$$

$$\ln \eta_{40^\circ\text{C}} = \ln(1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) - \frac{3.1556(20.0) + 1.925 \times 10^{-3}(400)}{149.0}$$

$$\ln \eta_{40^\circ\text{C}} = -6.905\,757\,276 - 0.428\,738\,255$$

$$\eta_{40^\circ\text{C}} = e^{-7.334\,495\,531}$$

$$\eta_{40^\circ\text{C}} = 6.526\,33 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\boxed{\eta_{40^\circ\text{C}} = 6.53 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}}$$

To find the activation energies, we use the definition

$$E_a = RT^2 \frac{d \ln \phi}{dT}$$

$$E_a = -RT^2 \frac{d \ln \eta}{dT}$$

From the empirical relationship, with

$$T = t + 273.15$$

$$\ln \eta_t = \ln \eta_{20^\circ\text{C}} - \frac{a(T - 293.15) + b(T - 293.15)^2}{T - 164.15}$$

$$\text{where } a = 3.1556, b = 1.925 \times 10^{-3}$$

$$\frac{d \ln \eta}{dT} = - \frac{(a + 2b(T - 293.15))(T - 164.15) - a(T - 293.15) - b(T - 293.15)^2}{(T - 164.15)^2}$$

$$\frac{d \ln \eta}{dT} = - \frac{(a + 2bT - 586.3b)(T - 164.15) - a(T - 293.15) - b(T - 293.15)^2}{(T - 164.15)^2}$$



a. At  $T = 20.0\text{ }^{\circ}\text{C}$ , the activation energy is,

$$E_a = (8.3145\text{ J K mol}^{-1})(293.15\text{ K})^2$$

$$\times \frac{(a + 2b(293.15\text{ K}) - 586.3b)(293.15\text{ K} - 164.15) - \cancel{a(293.15\text{ K} - 293.15)} - \cancel{b(293.15\text{ K} - 293.15)^2}}{(293.15\text{ K} - 164.15)^2}$$

$$E_a = (8.3145\text{ J K mol}^{-1})(293.15\text{ K})^2$$

$$\times \frac{(3.1556 + 2(1.925 \times 10^{-3})(293.15\text{ K}) - 586.3(1.925 \times 10^{-3}))(293.15\text{ K} - 164.15)}{(293.15\text{ K} - 164.15)^2}$$

$$E_a = 17\,478.6615\text{ J mol}^{-1}$$

$$\boxed{E_a = 17.5\text{ kJ mol}^{-1}}$$

b. At  $T = 100.0\text{ }^{\circ}\text{C}$ , the activation energy is,

$$E_a = (8.3145\text{ J K mol}^{-1})(373.15\text{ K})^2$$

$$\times \frac{(a + 2b(373.15) - 586.3b)(373.15 - 164.15) - a(373.15 - 293.15) - b(373.15 - 293.15)^2}{(373.15 - 164.15)^2}$$

$$E_a = 12\,168.606\,04\text{ J mol}^{-1}$$

$$\boxed{E_a = 12.2\text{ kJ mol}^{-1}}$$

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**\*19.9.** Consider a hypothetical gas in which the molecules have mass but no size and do not interact with each other.

- a. What would be the viscosity of such a gas?
- b. Suppose instead that the molecules have zero size but attract one another. What can you then say about the viscosity?
- c. If they repel one another, what would the viscosity be?
- d. Give a clear explanation of your conclusions in all three cases.

**Solution:**

Given: a – d

Required: clear explanations

- a. In a hypothetical gas in which the molecules have no size, there are no collisions and there no exchanges of momentum between molecules. If there are no forces between the molecules, two layers can move past each other freely, and the viscosity is zero.
- b. If the molecules have no size but attract one another, a force is required to move one layer past another. The gas will therefore have a viscosity. Increasing the temperature will increase the molecular speeds and will decrease the viscosity, as in a liquid.
- c. If the molecules have no size but repel one another, a force again will be required to move one layer past another. There will again be a viscosity, which decreases with increasing temperature.

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**19.10.** The molecular diameter of the helium atom is 0.225 nm. Estimate, at 0 °C and 101.325 kPa,

- a. the viscosity of the gas,
- b. the self-diffusion coefficient,
- c. the mean speed of the molecules,
- d. the mean free path,
- e. the collision frequency  $Z_A$ , and
- f. the collision density  $Z_{AA}$ .

**Solution:**

Given:  $d = 0.225$  nm,  $T = 0$  °C,  $P = 101.325$  kPa

Required:  $\eta$ ,  $D$ ,  $\bar{u}$ ,  $\lambda$ ,  $Z_A$ ,  $Z_{AA}$

a. To find viscosity, we use Eq. 19.16,

$$\eta = \frac{(mk_B T)^{1/2}}{\pi^{3/2} d^2} = \frac{(mk_B T)^{1/2}}{\pi^{1/2} \sigma}$$

For the helium atom, the mass is given by,

$$m = \frac{M}{N_A}$$

$$m = \frac{4.0026 \cancel{\text{g}} \cancel{\text{mol}^{-1}}}{6.022 \times 10^{23} \cancel{\text{mol}^{-1}}} \times 10^{-3} \text{ kg } \cancel{\text{g}^{-1}}$$

$$m = 6.646\,63 \times 10^{-27} \text{ kg}$$

Solving for  $\eta$  we get,

$$\eta = \frac{\left[ (6.646\,63 \times 10^{-27} \text{ kg}) (1.381 \times 10^{-23} \text{ J K}^{-1}) (273.15 \text{ K}) \right]^{1/2}}{\pi^{3/2} (0.225 \times 10^{-9} \text{ m})^2}$$

$$\eta = 1.77627 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$\boxed{\eta = 1.78 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}}$$

b. We calculate the self-diffusion coefficient from Eq. 19.57,

$$\eta = \rho D$$

$$D = \frac{\eta}{\rho}$$

$$\rho = \frac{mN}{V} = \frac{mP}{k_B T}$$

$$D = \frac{\eta k_B T}{mP}$$

$$D = \frac{(1.77627 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}) (1.381 \times 10^{-23} \text{ J K}^{-1}) (273.15 \text{ K})}{(6.646\,63 \times 10^{-27} \text{ kg}) (101\,325 \text{ Pa})}$$

$$D = 9.949\,13 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

$$\boxed{D = 9.95 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}}$$

c. We calculate  $\bar{u}$  from Table 1.3 as,

$$\bar{u} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}$$

$$\bar{u} = \sqrt{\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1})(273.15 \text{ K})}{\pi(6.646\,63 \times 10^{-27} \text{ kg})}}$$

$$\bar{u} = 1\,202.172\,472 \text{ m s}^{-1}$$

$$\boxed{\bar{u} = 1.20 \times 10^3 \text{ m s}^{-1}}$$

d. The mean free path is given in Chapter 1 by Eq. 1.68

$$\lambda = \frac{V}{\sqrt{2}\pi d_{\text{A}}^2 N_{\text{A}}}$$

From the ideal gas law,

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{V}{N} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{(101\,325 \text{ Pa})(6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$\frac{V}{N} = 3.722\,03 \times 10^{-26} \text{ m}^3$$

Therefore the mean free path is,

$$\lambda = \frac{3.722\,03 \times 10^{-26} \text{ m}^3}{\sqrt{2}\pi(0.225 \times 10^{-9} \text{ m})^2}$$

$$\lambda = 1.654817375 \times 10^{-7} \text{ m}$$

$$\boxed{\lambda = 1.65 \times 10^{-7} \text{ m}}$$

e. The expression for  $Z_{\text{A}}$  is also found in Chapter 1 as Eq. 1.66,

$$Z_A = \frac{\sqrt{2}\pi d_A^2 \bar{u}_A N_A}{V} \quad (\text{SI unit : s}^{-1})$$

Which we recognize as,

$$Z_A = \frac{\bar{u}_A}{\lambda}$$

$$Z_A = \frac{1\,202.172\,472 \cancel{\text{ m}} \text{ s}^{-1}}{1.654\,82 \times 10^{-7} \cancel{\text{ m}}}$$

$$Z_A = 7\,264\,683\,644 \text{ s}^{-1}$$

$$\boxed{Z_A = 7.26 \times 10^9 \text{ s}^{-1}}$$

f. From Eqs. 1.59 and 1.61,

$$Z_{AA} = \frac{1}{2} Z_A \frac{N}{V}$$

$$Z_{AA} = \frac{1}{2} (7\,264\,683\,644 \text{ s}^{-1}) (3.722\,03 \times 10^{-26} \text{ m}^3)^{-1}$$

$$Z_{AA} = 9.759\,03 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}$$

$$\boxed{Z_{AA} = 9.76 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}}$$

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**19.11.** Calculate the mean square distance traveled by a molecule of  $\text{H}_2$  at  $20^\circ\text{C}$  and  $101.325\text{ kPa}$  in  $10\text{ s}$  ( $D = 1.005 \times 10^{-4}\text{ m}^2\text{ s}^{-1}$ ).

**Solution:**

Given:  $\text{H}_2$  :  $P = 101.325\text{ kPa}$ ,  $t = 10\text{ s}$ ,  $D = 1.005 \times 10^{-4}\text{ m}^2\text{ s}^{-1}$

Required:  $\sqrt{\overline{x^2}}$

From Eq. 19.48, the mean square distance is given by,

$$\overline{x^2} = 2Dt$$

$$\sqrt{\overline{x^2}} = \sqrt{2Dt}$$

$$\sqrt{\overline{x^2}} = \sqrt{2(1.005 \times 10^{-4}\text{ m}^2\text{ s}^{-1})(10\text{ s})}$$

$$\sqrt{\overline{x^2}} = 0.044833024\text{ m}$$

$$\boxed{\sqrt{\overline{x^2}} = 4.5\text{ cm}}$$

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**19.12.** Solutions of (a) glucose ( $D = 6.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) and (b) tobacco mosaic virus ( $D = 5.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ) were maintained at a constant temperature of  $20^\circ\text{C}$  and without agitation for 100 days. How far would a given molecule of each be expected to diffuse in that time?

**Solution:**

Given:  $D_{\text{glucose}} = 6.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $D_{\text{virus}} = 5.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ,  $T = 20.0^\circ\text{C}$ ,  $t = 100 \text{ days}$

Required:  $\sqrt{x^2}$

From Eq. 19.48, the mean square distance is given by,

$$\overline{x^2} = 2Dt$$

$$\sqrt{\overline{x^2}} = \sqrt{2Dt}$$

Converting the time in days to time in seconds we can solve for the mean square distance,

$$t = 100 \times 24 \times 60 \times 60$$

$$t = 8\,640\,000 \text{ s}$$

$$\sqrt{\overline{x^2}}_{\text{glucose}} = \sqrt{2(6.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})(8\,640\,000 \text{ s})}$$

$$\sqrt{\overline{x^2}}_{\text{glucose}} = 0.108\,399\,262 \text{ m}$$

$$\boxed{\sqrt{\overline{x^2}}_{\text{glucose}} = 11 \text{ cm}}$$

For the virus,

$$\sqrt{\overline{x^2}}_{\text{virus}} = \sqrt{2(5.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1})(8\,640\,000 \text{ s})}$$

$$\sqrt{\overline{x^2}}_{\text{virus}} = 0.009\,569\,953 \text{ m}$$

$$\boxed{\sqrt{\overline{x^2}}_{\text{virus}} = 0.96 \text{ cm}}$$

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**19.13.** Estimate the diffusion coefficient of cupric sulfate in water at 25 °C from the molar conductivities given in Table 7.3 (p. 291).

**Solution:**

Given:  $T = 25\text{ °C}$ , Table 7.3

Required:  $D$

To solve this problem, we follow the example set by Example 19.4

Using Eq. 19.73, at 25 °C,

$$D = \frac{RT}{F^2 |z_i|} \lambda^\circ$$

$$D = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(96500 \text{ C mol}^{-1})^2 (2)} \lambda^\circ (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$$

$$D = 1.33103 \times 10^{-7} \lambda^\circ \text{ J } \Omega^{-1} \text{ C}^{-2} \text{ cm}^2$$

$$D = 1.33103 \times 10^{-7} \lambda^\circ \text{ cm}^2 \text{ s}^{-1}$$

From Table 7.3, we obtain the molar conductivities,

$$\lambda_{\frac{1}{2}\text{Cu}^{2+}} = 56.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\frac{1}{2}\text{SO}_4^{2-}} = 80.0 \text{ S cm}^2 \text{ mol}^{-1}$$

For  $\text{Cu}^{2+}$ ,

$$D_+ = (1.33103 \times 10^{-7})(56.6)$$

$$D_+ = 7.5336 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

For  $\text{SO}_4^{2-}$ ,

$$D_- = (1.331\,03 \times 10^{-7})(80.0)$$

$$D_- = 1.064\,82 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

Using Eq. 19.74,

$$D = \frac{2D_+D_-}{D_+ + D_-}$$

$$D = \frac{2 \times (7.533\,6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1})(1.064\,82 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})}{7.533\,6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} + 1.064\,82 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}}$$

$$D = 8.824\,13 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

$$\boxed{D = 8.82 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}}$$

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**19.14.** Estimate the diffusion coefficient of sodium acetate in water at 25 °C from the following mobility values:

$$\text{Na}^+: 5.19 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

$$\text{CH}_3\text{COO}^-: 4.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

**Solution:**

Given:  $T = 25^\circ\text{C}$ ,  $u_{e, \text{Na}^+} = 5.19 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $u_{e, \text{CH}_3\text{COO}^-} = 4.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  mobility

Required:  $D$

To solve this problem we use Eq. 19.72,

$$D = \frac{k_B T}{Q} u_i$$

Since the charge on 1 mole of an equivalent ion  $QL$ , is  $96\,500 \text{ C mol}^{-1}$ , we can write Eq. 19.72 as,

$$D = \frac{RT}{Q} u_e$$

$$D = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(96\,500 \text{ C mol}^{-1})} u_e$$

$$D = (0.025\,688\,789 \text{ V}) u_e$$

For  $\text{Na}^+$ ,

$$D_+ = (0.025\,688\,789 \text{ V})(5.19 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$$

$$D_+ = 1.333\,25 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

For  $\text{CH}_3\text{COO}^-$ ,

$$D_- = (0.025\,688\,789 \text{ V})(4.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$$

$$D_- = 1.089\,2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

Using Eq. 19.74,

$$D = \frac{2D_+D_-}{D_+ + D_-}$$

$$D = \frac{2 \times (1.333\,25 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})(1.089\,2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})}{1.333\,25 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} + 1.089\,2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}}$$

$$D = 1.198\,93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

$$\boxed{D = 1.20 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}}$$

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**19.15.** The diffusion coefficient for horse hemoglobin in water is  $6.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  at  $20^\circ \text{C}$ . The viscosity of water at  $20^\circ \text{C}$  is  $1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$  and the specific volume of the protein is  $0.75 \text{ cm}^3 \text{ g}^{-1}$ . Assume the hemoglobin molecule to be spherical and to obey Stokes's law, and estimate its radius and the molecular weight.

**Solution:**

Given:  $D = 6.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $T = 20^\circ \text{C}$ ,  $\eta = 1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ,  $V_{\text{specific}} = 0.75 \text{ cm}^3 \text{ g}^{-1}$

Required:  $r$ ,  $M$

Stokes law is given by Eq. 19.77 as,

$$D = \frac{k_B T}{6\pi r \eta}$$

Solving for  $r$ , the radius of the hemoglobin molecule we get,

$$r = \frac{k_B T}{6\pi \eta D}$$

$$r = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(293.15 \text{ K})}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})(6.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})}$$

$$r = 3.40231 \times 10^{-9} \text{ m}$$

$$\boxed{r = 3.4 \times 10^{-9} \text{ m} = 3.4 \text{ nm}}$$

To get the molar mass, we first calculate the volume, assuming the molecule is perfectly spherical.

$$V = \frac{4}{3} \pi r^3$$

$$V = \frac{4}{3} \pi (3.402\,31 \times 10^{-9} \text{ m})^3$$

$$V = 1.649\,72 \times 10^{-25} \text{ m}^3$$

$$M = \frac{V}{V_{\text{specific}}} N_{\text{A}}$$

$$M = \frac{1.649\,72 \times 10^{-25} \text{ m}^3}{0.75 \times 10^{-6} \text{ m}^3 \text{ g}^{-1}} (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$M = 132\,461.798\,1 \text{ g mol}^{-1}$$

$$\boxed{M = 1.3 \times 10^5 \text{ g mol}^{-1}}$$

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**19.16.** If the diffusion coefficient for insulin is  $8.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  at  $20^\circ \text{C}$ , estimate the mean time required for an insulin molecule to diffuse through a distance equal to the diameter of a typical living cell ( $\approx 10 \mu\text{m}$ ).

**Solution:**

Given:  $D = 8.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $T = 20^\circ \text{C}$ ,  $x = 10 \mu\text{m}$

Required:  $t$

The mean time can be obtained from From Eq. 19.48,

$$\overline{x^2} = 2Dt$$

$$t = \frac{\overline{x^2}}{2D}$$

$$t = \frac{(10 \times 10^{-6} \text{ m})^2}{2(8.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})}$$

$$t = 0.609\,756\,098 \text{ s}$$

$$\boxed{t = 0.61 \text{ s}}$$

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**\*19.17.** A colloidal particle is spherical and has a diameter of  $0.3\ \mu\text{m}$  and a density of  $1.18\ \text{g cm}^{-3}$ . Estimate how long it will take for the particle to diffuse through a distance of  $1\ \text{mm}$  in water at  $20\ ^\circ\text{C}$  ( $\eta = 1.002 \times 10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}$ ; the density of water at  $20\ ^\circ\text{C} = 0.998\ \text{g cm}^{-3}$ ). (See also Problem 19.21.)

**Solution:**

Given:  $d = 0.3\ \mu\text{m}$ ,  $\rho = 1.18\ \text{g cm}^{-3}$ ,  $x = 1\ \text{mm}$ ,  $T = 20\ ^\circ\text{C}$ ,

$$\eta = 1.002 \times 10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}, \rho_{\text{water}} = 1.18\ \text{g cm}^{-3}$$

Required:  $t$

The mean time can be obtained from Eq. 19.48,

$$\overline{x^2} = 2Dt$$

$$t = \frac{\overline{x^2}}{2D}$$

Stokes law gives  $D$  in Eq. 19.77 as,

$$D = \frac{k_B T}{6\pi r \eta}$$

$$r = \frac{d}{2} = 1.5 \times 10^{-7}\ \text{m}$$

$$D = \frac{(1.381 \times 10^{-23}\ \text{J K}^{-1})(293.15\ \text{K})}{6\pi(1.002 \times 10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1})(1.5 \times 10^{-7}\ \text{m})}$$

$$D = 1.428\ 97 \times 10^{-12}\ \text{m}^2\ \text{s}^{-1}$$



Solving for  $t$ , we get,

$$t = \frac{(10^{-3} \text{ m})^2}{2(1.42897 \times 10^{-12} \text{ m}^2 \text{ s}^{-1})}$$

$$t = 349\,902.085\,4 \text{ s}$$

$$\boxed{t = 3.5 \times 10^5 \text{ s}}$$

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**19.18.** Diphtheria toxin was found to have, at 20 °C, a sedimentation coefficient of 4.60 Svedbergs and a diffusion coefficient of  $5.96 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . The toxin has a specific volume of  $0.736 \text{ cm}^3 \text{ g}^{-1}$ , and the density of water at 20 °C is  $0.998 \text{ g cm}^{-3}$ . Estimate a value for the molecular weight of the toxin.

**Solution:**

Given:

$$T = 20 \text{ °C}, s = 4.60 \times 10^{-13} \text{ s}, D = 5.96 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}, V_{\text{specific}} = 0.736 \text{ cm}^3 \text{ g}^{-1}, \rho = 0.998 \text{ g cm}^{-3}$$

Required:  $M$

The molar mass is given by the Svedberg equation, Eq. 19.93,

$$M = \frac{RTs}{D(1 - V_2\rho)}$$

Substitution into this equation gives the molar weight of the toxin.

$$M = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})(4.60 \times 10^{-13} \text{ s})}{(5.96 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})\left(1 - (0.736 \text{ cm}^3 \text{ g}^{-1})(0.998 \text{ g cm}^{-3})\right)}$$

$$M = 70.862\,894\,28 \text{ J mol}^{-1} \text{ m}^{-2} \text{ s}^2$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$M = 70.9 \text{ kg mol}^{-1}$$

$$M = 70.9 \times 10^3 \text{ g mol}^{-1}$$

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**19.19.** A protein has a sedimentation coefficient of  $1.13 \times 10^{-12} \text{ s}^{-1}$  at  $25^\circ\text{C}$  and a diffusion coefficient of  $4.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The density of the protein is  $1.32 \text{ g cm}^{-3}$  and that of water at  $25^\circ\text{C}$  is  $0.997 \text{ g cm}^{-3}$ . Calculate the molecular weight of the protein.

**Solution:**

Given:

$$T = 25^\circ\text{C}, s = 1.13 \times 10^{-12} \text{ s}, D = 4.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}, \rho_{\text{protein}} = 1.32 \text{ g cm}^{-3}, \rho_{\text{H}_2\text{O}} = 0.997 \text{ g cm}^{-3}$$

Required:  $M$

We solve this problem in the same manner as Problem 19.18, making the substitution for  $V_2$  as  $\frac{1}{\rho_{\text{protein}}}$ .

The molar mass is given by the Svedberg equation, Eq. 19.93,

$$M = \frac{RTs}{D(1 - V_2\rho)}$$

Substitution into this equation gives the molar weight of the protein .

$$M = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})(1.13 \times 10^{-12} \text{ s})}{(4.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}) \left( 1 - \frac{(0.997 \text{ g cm}^{-3})}{1.32 \text{ g cm}^{-3}} \right)}$$

$$M = 272.5658949 \text{ kg mol}^{-1}$$

$$\boxed{M = 2.7 \times 10^5 \text{ g mol}^{-1}}$$

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**\*19.20.** A protein of molecular weight 60 000 has a density of  $1.31 \text{ g cm}^{-3}$  and in water at  $25^\circ\text{C}$  ( $\rho = 0.997 \text{ g cm}^{-3}$ ;  $\eta = 8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ ) it has a sedimentation coefficient of  $4.1 \times 10^{-13} \text{ s}^{-1}$ . Calculate the frictional coefficient  $f$

a. from the sedimentation coefficient, and

b. by the use of Stokes's law.

Suggest a reason why the two values are not quite the same.

**Solution:**

Given:  $T = 25^\circ\text{C}$ ,  $M = 60\,000 \text{ g mol}^{-1}$ ,  $\rho_{\text{protein}} = 1.31 \text{ g cm}^{-3}$ ,  $s = 4.1 \times 10^{-11} \text{ s}^{-1}$ ,

$\rho_{\text{H}_2\text{O}} = 0.997 \text{ g cm}^{-3}$ ,  $\eta = 8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

Required:  $f$  from a and b

a. To calculate the frictional coefficient from the sedimentation coefficient, we use Eq. 19.86,

$$v = \frac{(1 - V_2\rho)m\omega^2 x}{f}, \text{ where } s = \frac{v}{\omega^2 x} \text{ from Eq. 19.87.}$$

Therefore we get the frictional coefficient as,

$$s = \frac{(1 - V_2\rho)m}{f}$$

$$f = \frac{(1 - V_2\rho)m}{s}$$

To solve for  $f$  we first calculate the mass of the protein.

$$m = \frac{M}{N_A}$$

$$m = \frac{60.000 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$m = 9.96347 \times 10^{-23} \text{ kg}$$

Using the substitution for  $V_2$  as  $\frac{1}{\rho_{\text{protein}}}$ .

$$f = \frac{\left(1 - \frac{(0.997 \text{ g cm}^{-3})}{1.31 \text{ g cm}^{-3}}\right) (9.96347 \times 10^{-23} \text{ kg})}{4.1 \times 10^{-13} \text{ s}^{-1}}$$

$$f = 5.8063 \times 10^{-11} \text{ kg s}^{-1}$$

$$\boxed{f = 5.8 \times 10^{-11} \text{ kg s}^{-1}}$$

b. To solve for the frictional coefficient from Stokes Law, we use Eq. 19.76,

$$f = 6\pi r\eta$$

We assume the protein is perfectly spherical and use the volume of the sphere to find  $r$ .

$$V = \frac{m}{\rho}$$

$$V = \frac{9.96347 \times 10^{-23} \text{ kg}}{1.31 \times 10^3 \text{ kg m}^{-3}}$$

$$V = 7.6057 \times 10^{-26} \text{ m}^3$$

$$V = \frac{4}{3}\pi r^3$$

$$r = \left(\frac{3V}{4\pi}\right)^{1/3}$$

$$r = \left(\frac{3 \times 7.6057 \times 10^{-26} \text{ m}^3}{4\pi}\right)^{1/3}$$

$$r = 2.62835 \times 10^{-9} \text{ m}$$

Using  $r$ , we now solve for  $f$ .

$$f = 6\pi(2.628\,35 \times 10^{-9} \text{ m})(8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1})$$

$$f = 4.427\,68 \times 10^{-11} \text{ kg s}^{-1}$$

$$\boxed{f = 4.43 \times 10^{-11} \text{ kg s}^{-1}}$$

The two values are not quite the same since in the Stokes calculation, we assumed that the molecule is perfectly spherical.

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**\*19.21.** How long will it take the particle from Problem 19.17 to sediment a distance of 1 mm in the earth's gravitational field ( $g = 9.81 \text{ m s}^{-2}$ )?

**Solution:**

Given: Problem 19.17,  $x = 1 \text{ mm}$ ,  $g = 9.81 \text{ m s}^{-2}$

Required:  $t$

The limiting rate of sedimentation is given by Eq. 19.85 as,

$$v = \frac{(1 - V_2 \rho) mg}{6\pi r \eta}$$

To solve for  $v$  we first calculate the mass of the particle using volume and density,

$$\rho = \frac{m}{V}$$

$$m = \left( \frac{4}{3} \pi r^3 \right) \rho$$

$$m = \frac{4}{3} \pi (1.5 \times 10^{-7} \text{ m})^3 (1.18 \times 10^3 \text{ kg m}^{-3})$$

$$m = 1.66819 \times 10^{-17} \text{ kg}$$

The speed is therefore,

$$v = \frac{\left( 1 - \frac{0.998 \text{ g cm}^{-3}}{1.18 \text{ g cm}^{-3}} \right) (1.66819 \times 10^{-17} \text{ kg}) (9.81 \text{ m s}^{-2})}{6\pi (1.5 \times 10^{-7} \text{ m}) (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})}$$

$$v = 8.90928 \times 10^{-9} \text{ m s}^{-1}$$

Since speed is the distance travelled over time, the particle sediments a distance of 1 mm in,

$$v = \frac{d}{t}$$

$$t = \frac{d}{v}$$

$$t = \frac{1 \times 10^{-3} \text{ m}}{8.909 \, 28 \times 10^{-9} \text{ m s}^{-1}}$$

$$t = 112 \, 242.497 \, 6 \text{ s}$$

$$t = 1.12 \times 10^5 \text{ s}$$

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**\*19.22.** An aqueous colloidal solution contains spherical particles of uniform size and of density  $1.33 \text{ g cm}^{-3}$ . The diffusion coefficient at  $25^\circ\text{C}$  is  $1.20 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ; make an estimate of the sedimentation coefficient ( $\rho(\text{H}_2\text{O}) = 0.997 \text{ g cm}^{-3}$ ;  $\eta(\text{H}_2\text{O}) = 8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ ).

**Solution:**

Given:  $d = 1.33 \text{ g cm}^{-3}$ ,  $T = 25^\circ\text{C}$ ,  $D = 1.20 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  
 $\rho_{\text{H}_2\text{O}} = 0.997 \text{ g cm}^{-3}$ ,  $\eta_{\text{H}_2\text{O}} = 8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

Required:  $s$

To find the sedimentation coefficient, we will use Eq. 19.89,

$$s = \frac{(1 - V_2 \rho)m}{6\pi\eta r}$$

We find the radius using Stokes Law, Eq. 19.77,

$$D = \frac{k_B T}{6\pi r \eta}$$

$$r = \frac{k_B T}{6\pi \eta D}$$

$$r = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}{6\pi (8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1})(1.20 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})}$$

$$r = 2.03683 \times 10^{-8} \text{ m}$$

The mass of each particle is calculated using volume and density,

$$\rho = \frac{m}{V}$$

$$m = \left( \frac{4}{3} \pi r^3 \right) \rho$$

$$m = \frac{4}{3} \pi (2.03683 \times 10^{-8} \text{ m})^3 (1.33 \times 10^3 \text{ kg m}^{-3})$$

$$m = 4.70764 \times 10^{-20} \text{ kg}$$

The sedimentation coefficient is,

$$s = \frac{\left( 1 - \frac{0.997 \text{ g cm}^{-3}}{1.33 \text{ g cm}^{-3}} \right) (4.70764 \times 10^{-20} \text{ kg})}{6\pi (8.937 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}) (2.03683 \times 10^{-8} \text{ m})}$$

$$s = 3.43517 \times 10^{-11} \text{ s}$$

$$\boxed{s = 3.44 \times 10^{-11} \text{ s}}$$

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**19.23.** At 20 °C,  $\gamma$ -globulin has a sedimentation constant of  $7.75 \times 10^{-13}$  s, a diffusion coefficient in water of  $4.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , and a density of  $1.353 \text{ g cm}^{-3}$ . The density of water at 20 °C is  $0.998 \text{ g cm}^{-3}$ .

a. Estimate the molecular weight of  $\gamma$ -globulin.

b. Assuming the Stokes-Einstein equation to apply, estimate the radius of the protein molecule. The viscosity of water at 20 °C is  $1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ .

**Solution:**

Given:  $T = 20 \text{ °C}$ ,  $s = 7.75 \times 10^{-13} \text{ s}$ ,  $D = 4.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $\rho = 1.353 \text{ g cm}^{-3}$ ,

$\rho_{\text{H}_2\text{O}} = 0.998 \text{ g cm}^{-3}$ ,  $\eta = 1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$

Required:  $M$ ,  $r$

a. We solve this problem in the same manner as Problem 19.18, making the substitution for  $V_2$  as  $\frac{1}{\rho}$ .

The molar mass is given by the Svedberg equation, Eq. 19.93,

$$M = \frac{RTs}{D(1 - V_2\rho)}$$

Substitution into this equation gives the molar weight of the protein .

$$M = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})(7.75 \times 10^{-13} \text{ s})}{(4.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}) \left( 1 - \frac{(0.998 \text{ g cm}^{-3})}{1.353 \text{ g cm}^{-3}} \right)}$$

$$M = 149.987 \, 803 \, 4 \text{ kg mol}^{-1}$$

$$\boxed{M = 1.5 \times 10^5 \text{ g mol}^{-1}}$$

b. To estimate radius, we use the Stokes-Einstein equation, Eq.19.77

$$D = \frac{k_B T}{6\pi r \eta}$$

$$r = \frac{k_B T}{6\pi \eta D}$$

$$r = \frac{(1.381 \times 10^{-23} \text{ J } \cancel{\text{K}^{-1}})(293.15 \cancel{\text{K}})}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})(4.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})}$$

$$r = 4.46553 \times 10^{-9} \text{ m}$$

$$\boxed{r = 4.5 \times 10^{-9} \text{ m}}$$

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**\*19.24.** A sample of human hemoglobin had a sedimentation constant of 4.48 Svedbergs in water at 20 °C and a diffusion coefficient of  $6.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The specific volume of human hemoglobin is  $0.749 \text{ cm}^3 \text{ g}^{-1}$ , and the density of water at 20 °C is  $0.998 \text{ g cm}^{-3}$ .

- Estimate the molecular weight of human hemoglobin.
- How far would a molecule diffuse in 1 minute?
- Neglect diffusion and estimate how far a molecule would sediment in 1 minute.
- In a centrifuge rotating at 15 000 rpm, how far would a molecule sediment in 1 minute if it were 20 cm from the center of rotation?
- Assume the molecule to be spherical and estimate its radius by the use of the Stokes-Einstein equation.
- Estimate the radius from the molecular weight and the density.

**Solution:**

Given:  $T = 20 \text{ °C}$ ,  $s = 4.48 \times 10^{-13} \text{ s}$ ,  $D = 6.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $V_2 = 0.749 \text{ cm}^3 \text{ g}^{-1}$ ,  $\rho_{\text{H}_2\text{O}} = 0.998 \text{ g cm}^{-3}$

Required: a – f

To solve this problem, we can refer to Example 19.6 for extra help.

- a. The molar mass is obtained from Eq. 19.93,

$$M = \frac{RTs}{D(1 - V_2\rho)}$$

$$M = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})(4.48 \times 10^{-13} \text{ s})}{(6.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})\left(1 - (0.749 \text{ cm}^3 \text{ g}^{-1})(0.998 \text{ g cm}^{-3})\right)}$$

$$M = 62.675\,385\,94 \text{ J mol}^{-1} \text{ m}^{-2} \text{ s}^2$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$M = 62.7 \text{ kg mol}^{-1}$$

$$\boxed{M = 62.7 \times 10^3 \text{ g mol}^{-1}}$$

b. Using Einstein's equation, Eq. 19.48, the molecule would diffuse,

$$\overline{x^2} = 2Dt$$

$$\sqrt{\overline{x^2}} = \sqrt{2Dt}$$

$$\sqrt{\overline{x^2}} = \sqrt{2(6.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})(60 \text{ s})}$$

$$\sqrt{\overline{x^2}} = 9.09945 \times 10^{-5} \text{ m}$$

$$\boxed{\sqrt{\overline{x^2}} = 9.1 \times 10^{-5} \text{ m}}$$

c. The sedimentation coefficient is the rate of sedimentation for an acceleration of gravity of unity. In a gravitational field of  $g = 9.8 \text{ m s}^{-2}$  the rate of sedimentation is,

$$v = 9.81 \text{ m s}^{-2} \times 4.48 \times 10^{-13} \text{ s}$$

$$v = 4.39488 \times 10^{-12} \text{ m s}^{-1}$$

Therefore the distance travelled is,

$$d = vt$$

$$d = (4.39488 \times 10^{-12} \text{ m s}^{-1})(60 \text{ s})$$

$$d = 2.63693 \times 10^{-10} \text{ m}$$

$$\boxed{d = 2.64 \times 10^{-10} \text{ m}}$$

d. The rate of sedimentation in an ultracentrifuge is given by Eq. 19.87

$$v = s\omega^2 x$$

The speed of revolution  $\omega$  is

$$\omega = \left( \frac{15000 \text{ rpm}}{60 \text{ s min}^{-1}} \right) \times 2\pi$$

$$\omega = 1570.796327 \text{ rad s}^{-1}$$

The rate of sedimentation, with  $x = 20$  cm is,

$$v = (4.48 \times 10^{-13} \text{ s}) (1570.796327 \text{ rad s}^{-1})^2 (0.2 \text{ m})$$

$$v = 2.21079 \times 10^{-7} \text{ m s}^{-1}$$

Therefore the distance travelled is,

$$d = vt$$

$$d = (2.21079 \times 10^{-7} \text{ m s}^{-1}) (60 \text{ s})$$

$$d = 1.32647 \times 10^{-5} \text{ m}$$

$$\boxed{d = 1.33 \times 10^{-5} \text{ m}}$$

e. To estimate radius, we use the Stokes-Einstein equation, Eq.19.77

$$D = \frac{k_B T}{6\pi r \eta}$$

$$r = \frac{k_B T}{6\pi \eta D}$$

$$r = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) (293.15 \text{ K})}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) (6.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})}$$

$$r = 3.10646 \times 10^{-9} \text{ m}$$

$$\boxed{r = 3.1 \times 10^{-9} \text{ m}}$$

f. Using molecular weight and the density we can make another estimate for the radius. The mass of the molecule is given by,

$$m = \frac{M}{N_A}$$

$$m = \frac{62.675\,385\,94\,\text{kg mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}}$$

$$m = 1.040\,77 \times 10^{-22}\,\text{kg}$$

Using density,

$$V = \frac{m}{\rho}$$

$$V = (1.040\,77 \times 10^{-19}\,\cancel{\text{g}}) (0.749 \times 10^{-6}\,\text{m}^3\,\cancel{\text{g}}^{-1})$$

$$V = 7.795\,39 \times 10^{-29}\,\text{m}^3$$

$$V = \frac{4}{3}\pi r^3$$

$$r = \left( \frac{3V}{4\pi} \right)^{1/3}$$

$$r = \left( \frac{3 \times 7.795\,39 \times 10^{-29}\,\text{m}^3}{4\pi} \right)^{1/3}$$

$$r = 2.650\,02 \times 10^{-10}\,\text{m}$$

$$\boxed{r = 2.65 \times 10^{-10}\,\text{m}}$$

This is in reasonable agreement with the radius obtained in part e. The molecule is not in fact spherical, and the equation is more satisfactory for larger particles.

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**\*19.25.** In the first decade of the twentieth century Jean Perrin carried out important investigations on the sedimentation, in the gravitational field, of particles of gamboge, mastic, and other paint pigments. Consider particles of density  $1.2 \text{ g cm}^{-3}$  and of the following radii:

- a. 1 mm
- b. 0.1 mm
- c.  $10 \mu\text{m}$
- d.  $1 \mu\text{m}$
- e. 10 nm

In each case, assuming Stokes's law to apply, estimate the distance the particle would sediment in 1 hour, in water at  $20^\circ\text{C}$  (viscosity,  $\eta = 1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$  and density  $0.998 \text{ g cm}^{-3}$ ).

f. In the case of the particle having a radius of 10 nm, what speed of rotation in an ultracentrifuge would be required to bring about a sedimentation of 1 mm in 1 hour? Take the distance from the axis of rotation to be 10 cm.

**Solution:**

Given:  $\rho = 1.2 \text{ g cm}^{-3}$ ,  $r, t = 1 \text{ h}$ ,  $T = 20^\circ\text{C}$ ,  $\eta = 1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ,  $\rho_{\text{water}} = 0.998 \text{ g cm}^{-3}$

Required:  $d$ ,  $v$

a. To solve for the distance travelled, we need to calculate the sedimentation coefficient, given by Eq. 19.89,

$$s = \frac{(1 - V_2 \rho)m}{6\pi\eta r}$$

The mass of the particle is calculated as,

$$m = V\rho$$

$$m = \frac{4}{3}\pi r^3 \rho$$

$$m = \frac{4}{3}\pi (1 \times 10^{-3} \text{ m})^3 (1.2 \text{ g cm}^{-3} = 1200 \text{ kg m}^{-3})$$

$$m = 5.02655 \times 10^{-6} \text{ kg}$$

Making the substitution for  $V_2$  as  $\frac{1}{\rho}$ , the sedimentation coefficient is,

$$s = \frac{\left(1 - \frac{0.998 \text{ g cm}^{-3}}{1.2 \text{ g cm}^{-3}}\right) (5.02655 \times 10^{-6} \text{ kg})}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) (1 \times 10^{-3} \text{ m})}$$

$$s = 0.04479929 \text{ s}$$

The rate of sedimentation in a gravitational field is therefore,

$$v = 9.81 \text{ m s}^{-2} \times 0.04479929 \text{ s}$$

$$v = 0.439481038 \text{ m s}^{-1}$$

Therefore the distance travelled is,

$$d = vt$$

$$d = (0.439481038 \text{ m s}^{-1}) (3600 \text{ s})$$

$$d = 1582.131737 \text{ m}$$

$$\boxed{d = 1.58 \times 10^3 \text{ m}}$$

Repeating the same procedure for b – e we can solve for the distance of sedimentation.

b.

$$m = \frac{4}{3} \pi (0.1 \times 10^{-3} \text{ m})^3 (1200 \text{ kg m}^{-3})$$

$$m = 5.026\,55 \times 10^{-9} \text{ kg}$$

$$s = \frac{\left(1 - \frac{0.998 \text{ g cm}^{-3}}{1.2 \text{ g cm}^{-3}}\right) (5.026\,55 \times 10^{-9} \text{ kg})}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) (0.1 \times 10^{-3} \text{ m})}$$

$$s = 4.479\,929 \times 10^{-4} \text{ s}$$

The rate of sedimentation in a gravitational field is therefore,

$$v = 9.81 \text{ m s}^{-2} \times 4.479\,929 \times 10^{-4} \text{ s}$$

$$v = 4.394\,8103\,8 \times 10^{-3} \text{ m s}^{-1}$$

Therefore the distance travelled is,

$$d = (4.394\,8103\,8 \times 10^{-3} \text{ m s}^{-1}) (3600 \text{ s})$$

$$d = 15.821\,317\,37 \text{ m}$$

$$\boxed{d = 15.8 \text{ m}}$$

c.

$$m = \frac{4}{3} \pi (10 \times 10^{-6} \text{ m})^3 (1200 \text{ kg m}^{-3})$$

$$m = 5.026\,548\,246 \times 10^{-12} \text{ kg}$$

$$s = \frac{\left(1 - \frac{0.998 \text{ g cm}^{-3}}{1.2 \text{ g cm}^{-3}}\right) 5.026\,548\,246 \times 10^{-12} \text{ kg}}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) (10 \times 10^{-6} \text{ m})}$$

$$s = 4.479\,929\,031 \times 10^{-6} \text{ s}$$

The rate of sedimentation in a gravitational field is therefore,

$$v = 9.81 \text{ m s}^{-2} \times 4.479\,929\,031 \times 10^{-6} \text{ s}$$

$$v = 9.394\,810\,379 \times 10^{-5} \text{ m s}^{-1}$$

Therefore the distance travelled is,

$$d = (4.394\,8103\,8 \times 10^{-5} \text{ m } \cancel{\text{s}^{-1}}) (3600 \cancel{\text{s}})$$

$$d = 0.158\,213\,2 \text{ m}$$

$$\boxed{d = 1.58 \times 10^{-1} \text{ m}}$$

d.

$$m = \frac{4}{3} \pi (1 \times 10^{-6} \text{ m})^3 (1200 \text{ kg m}^{-3})$$

$$m = 5.026\,55 \times 10^{-15} \text{ kg}$$

$$s = \frac{\left(1 - \frac{0.998 \cancel{\text{g cm}^{-3}}}{1.2 \cancel{\text{g cm}^{-3}}}\right) (5.026\,55 \times 10^{-15} \cancel{\text{kg}})}{6\pi (1.002 \times 10^{-3} \cancel{\text{kg m}^{-1} \text{s}^{-1}}) (1 \times 10^{-6} \cancel{\text{m}})}$$

$$s = 4.479\,929 \times 10^{-8} \text{ s}$$

The rate of sedimentation in a gravitational field is therefore,

$$v = 9.81 \text{ m s}^{-2} \times 4.479\,929 \times 10^{-8} \text{ s}$$

$$v = 4.394\,8103\,8 \times 10^{-7} \text{ m s}^{-1}$$

Therefore the distance travelled is,

$$d = (4.394\,8103\,8 \times 10^{-7} \text{ m } \cancel{\text{s}^{-1}}) (3600 \cancel{\text{s}})$$

$$d = 0.001\,582\,132 \text{ m}$$

$$\boxed{d = 1.58 \times 10^{-3} \text{ m}}$$

e.

$$m = \frac{4}{3} \pi (10 \times 10^{-9} \text{ m})^3 (1200 \text{ kg m}^{-3})$$

$$m = 5.026\,55 \times 10^{-21} \text{ kg}$$

$$s = \frac{\left(1 - \frac{0.998 \text{ g cm}^{-3}}{1.2 \text{ g cm}^{-3}}\right) (5.026\,55 \times 10^{-21} \text{ kg})}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) (10 \times 10^{-9} \text{ m})}$$

$$s = 4.479\,929 \times 10^{-12} \text{ s}$$

The rate of sedimentation in a gravitational field is therefore,

$$v = 9.81 \text{ m s}^{-2} \times 4.479\,929 \times 10^{-12} \text{ s}$$

$$v = 4.394\,8103\,8 \times 10^{-11} \text{ m s}^{-1}$$

Therefore the distance travelled is,

$$d = (4.394\,8103\,8 \times 10^{-11} \text{ m s}^{-1}) (3600 \text{ s})$$

$$d = 1.582\,13 \times 10^{-7} \text{ m}$$

$$\boxed{d = 1.58 \times 10^{-7} \text{ m}}$$

f. The rate of sedimentation in an ultracentrifuge is given by Eq. 19.87

$$v = s\omega^2 x$$

The rate of sedimentation is,

$$v = \frac{1 \times 10^{-3} \text{ m}}{3600 \text{ s}}$$

$$v = 2.777\,78 \times 10^{-7} \text{ m s}^{-1}$$

The sedimentation coefficient is calculated as,

$$m = \frac{4}{3} \pi (10 \times 10^{-9} \text{ m})^3 (1200 \text{ kg m}^{-3})$$

$$m = 5.026\,55 \times 10^{-21} \text{ kg}$$

$$s = \frac{\left(1 - \frac{0.998 \text{ g cm}^{-3}}{1.2 \text{ g cm}^{-3}}\right) (5.026\,55 \times 10^{-21} \text{ kg})}{6\pi (1.002 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) (10 \times 10^{-9} \text{ m})}$$

$$s = 4.479\,929 \times 10^{-12} \text{ s}$$

This leads to,

$$\omega = \sqrt{\frac{v}{sx}}$$

$$\omega = \sqrt{\frac{2.777\,78 \times 10^{-7} \text{ m s}^{-1}}{(4.479\,929 \times 10^{-12} \text{ s}) (10 \times 10^{-3} \text{ m})}}$$

$$\omega = 2490.079\,326 \text{ rad s}^{-1}$$

$$\frac{\omega}{2\pi} \text{ (revolutions per second)}$$

$$= 396.308\,4334 \text{ rps}$$

$$= 23\,778.506 \text{ rpm}$$

$$\boxed{2.38 \times 10^4 \text{ rpm}}$$

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**\*19.26.** Perrin also carried out, using pigment particles, experiments on Brownian movement in which he determined distances traveled by individual particles in various periods of time. For each of the particles of five different radii mentioned in the previous problem, estimate the diffusion coefficient and the average distance traveled in 1 hour. Take the water temperature again as 20°C and use the data of Problem 19.25.

**Solution:**

Given: Problem 19.25

Required:  $D$ ,  $\sqrt{x^2}$

The diffusion coefficient is given by Eq. 19.77 as,

$$D = \frac{k_B T}{6\pi r \eta}$$

Solving using the data from part a of the previous question we get,

$$D = \frac{k_B T}{6\pi r \eta}$$

$$D = \frac{(1.381 \times 10^{-23} \text{ J } \cancel{\text{K}^{-1}})(293.15 \cancel{\text{K}})}{6\pi (1.002 \times 10^{-3} \text{ kg } \cancel{\text{m}^{-1}} \text{ s}^{-1})(10 \times 10^{-3} \cancel{\text{m}})}$$

$$D = 2.143 \, 46 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$$

$$\boxed{D = 2.143 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}}$$

Using Einstein's equation, Eq. 19.48,

$$\overline{x^2} = 2Dt$$

$$\sqrt{\overline{x^2}} = \sqrt{2Dt}$$

$$\sqrt{\overline{x^2}} = \sqrt{2(2.143\,46 \times 10^{-16} \text{ m}^2 \text{ s}^{-1})(3600 \text{ s})}$$

$$\sqrt{\overline{x^2}} = 1.242\,29 \times 10^{-6} \text{ m}$$

$$\boxed{\sqrt{\overline{x^2}} = 1.242 \times 10^{-6} \text{ m}}$$

Repeating the above procedure for b – e, we summarize with the following results,

	$r / \text{m}$	$D \times 10^{-16} / \text{m}^2 \text{ s}^{-1}$	$\sqrt{\overline{x^2}} / \mu\text{m}$
a.	$10^{-3}$	2.143	1.242
b.	$10^{-4}$	21.43	3.928
c.	$10^{-5}$	214.3	12.42
d.	$10^{-6}$	2143	39.28
e.	$10^{-8}$	$2.143 \times 10^5$	392.8

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**\*19.27.** A pure protein in water is centrifuged to equilibrium at 25 °C and at 25 000 rpm. At distances of 8.34 cm and 9.12 cm from the axis of rotation the concentrations of the protein are measured to be 3.52 g cm<sup>-3</sup> and 22.49 g cm<sup>-3</sup>, respectively. The specific volume  $V_1$  of the protein is 0.78 cm<sup>3</sup> g<sup>-1</sup>, and the density of water at 25 °C is 0.997 g cm<sup>-3</sup>. Calculate the molecular weight of the protein.

**Solution:**

Given:  $T = 25\text{ °C}$ , 25 000 rpm,  $x_1 = 8.34\text{ cm}$ ,  $x_2 = 9.12\text{ cm}$ ,  $\rho_1 = 3.52\text{ g cm}^{-3}$ ,  $\rho_2 = 22.49\text{ g cm}^{-3}$

$$V_1 = 0.78\text{ cm}^3\text{ g}^{-1}, \rho_{\text{water}} = 0.997\text{ g cm}^{-3}$$

Required:  $M$

We can calculate the molecular weight from Eq. 19.98,

$$M = \frac{2RT \ln(c_2/c_1)}{(1 - V_2\rho)\omega^2(x_2^2 - x_1^2)}$$

Solving for  $\omega$  we get,

$$\omega = \frac{25\,000\text{ rpm}}{60\text{ s min}^{-1}} \times 2\pi$$

$$\omega = 2617.993\,878\text{ rad s}^{-1}$$

Taking the density of the protein as a measure of the concentration, we solve.]

$$M = \frac{2 \left( 8.3145\text{ J K}^{-1}\text{ mol}^{-1} \right) (298.15\text{ K}) \ln \left( \frac{22.49\text{ g cm}^{-3}}{3.52\text{ g cm}^{-3}} \right)}{\left( 1 - \left( 0.78\text{ cm}^3\text{ g}^{-1} \right) \left( 0.997\text{ g cm}^{-3} \right) \right) \left( 2617.993\,878\text{ rad s}^{-1} \right)^2 \left( \left( 9.12 \times 10^{-2}\text{ m} \right)^2 - \left( 8.34 \times 10^{-2}\text{ m} \right)^2 \right)}$$

$$M = 4.430\,571\,965\text{ kg mol}^{-1}$$

$$M = 4430.571\,965\text{ g mol}^{-1}$$

$$\boxed{M = 4.43 \times 10^3\text{ g mol}^{-1}}$$

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**\*19.28.** A protein has a molecular weight of 1 000 000 and a specific volume of  $0.81 \text{ cm}^3 \text{ g}^{-1}$ . In an ultracentrifuge at  $25^\circ\text{C}$ , what speed of revolution is required to produce at equilibrium a concentration ratio of 20/1 at distances 10.00 cm and 9.00 cm from the axis of revolution? The density of water at  $25^\circ\text{C}$  is  $0.997 \text{ g cm}^{-3}$ .

**Solution:**

Given:  $M = 10^6 \text{ g mol}^{-1}$ ,  $V_2 = 0.81 \text{ cm}^3 \text{ g}^{-1}$ ,  $T = 25^\circ\text{C}$ ,  $c_2/c_1 = 20/1$ ,  $x_1 = 10.00 \text{ cm}$ ,  $x_2 = 9.00 \text{ cm}$

$$\rho_{\text{water}} = 0.997 \text{ g cm}^{-3}$$

Required:  $\omega$

We can solve for  $\omega$  using Eq. 19.98,

$$M = \frac{2RT \ln(c_2/c_1)}{(1 - V_2\rho)\omega^2(x_2^2 - x_1^2)}$$

$$\omega = \sqrt{\frac{2RT \ln(c_2/c_1)}{(1 - V_2\rho)M(x_2^2 - x_1^2)}}$$

$$\omega = \sqrt{\frac{2(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})\ln(20)}{\left(1 - (0.81 \text{ cm}^3 \text{ g}^{-1})(0.997 \text{ g cm}^{-3})\right)(10^3 \text{ kg mol}^{-1})\left((10.00 \times 10^{-2} \text{ m})^2 - (9.00 \times 10^{-2} \text{ m})^2\right)}}$$

$$\omega = 201.552\,775\,1 \text{ rad s}^{-1}$$

in rpm,

$$\omega = \frac{(201.552\,775\,1 \text{ rad s}^{-1}) \times 60 \text{ s}}{2\pi}$$

$$\omega = 1924.687\,227 \text{ rpm}$$

$$\boxed{\omega = 1.9 \times 10^3 \text{ rpm}}$$

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